BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1937.

Method of representing [electromagnetic moments and mesomerism in] organic compounds. A. CORNILLOT (Compt. rend., 1937, **204**, 694—697).—A scheme for diagrammatic representation of electromagnetic dipoles and mesomeric structures in simple org. compounds. E. W. W.

Formation of graphite in the pyrolysis of organic compounds.—See A., I, 321.

Reactions between atomic deuterium and saturated aliphatic hydrocarbons.—See A., I, 313.

Mercury-sensitised reactions of methane, deuteromethane, and the hydrogen isotopes.—See A., I, 317.

Analysis of saturated and unsaturated gaseous hydrocarbons at very low pressure. R. DELAPLACE (Compt. rend., 1937, **204**, 768—770).—A method of separating mixtures of C_2H_6, C_3H_8, *n*- and *iso*-C_4H_{10}, C_2H_4, C_3H_6, Δ^α- and *iso*-C_4H_8, and C_2H_2, using low-pressure fractionation followed by chemical separation, is discussed. A. J. E. W.

Photo-iodination of the butenes, propylene, and ethylene at low temperatures. Preparation and photolysis of αβ-di-iodobutane.—See A., I, 318.

Influence of admixtures on polymerisation of butadiene in presence of sodium.—See A., I, 315.

"True" and "conjunct" catalytic polymerisation of olefines. V. N. IPATIEV (Trans. Electrochem. Soc., 1937, **71**, Preprint 27, 313—321).—The author's work on the effect of temp., pressure, and concn. on the polymerisation of olefines chiefly by H_3PO_4 and H_2SO_4 is discussed with reference to the formation of (1) polymerides of the reactant ("true polymerisation") and (2) mixtures of products of different types ("conjunct polymerisation"). J. G. A. G.

"Hydro-polymerisation." V. N. IPATIEV and V. I. KOMAREVSKI (J. Amer. Chem. Soc., 1937, **59**, 720—722).—Hydrogenation of $CMe_2{:}CHMe$ or *iso*butene at 300°/80 kg. per sq. cm. in presence of Fe–NiO and metallic salts ($MgCl_2$, $AlCl_3$, $ZnCl_2$) or H_3PO_4 gives an *iso*decane, probably $CMe_2Et{\cdot}CHMePr^\alpha$, or *iso*octane, $CH_2Pr^\beta Bu^\gamma$, respectively. In absence of the salt or H_3PO_4 normal hydrogenation occurs. In absence of Fe–NiO neither hydrogenation nor polymerisation occurs. This simultaneous occurrence of both reactions is termed "hydro-polymerisation." R. S. C.

Fission and isomerisation of olefines. III. Fission of *as*-di*tert.*-alkylethylenes and isomerisation of *tert.*-alkylvinyl radicals of the general type $CR_3{\cdot}\dot{C}{:}CH_2$. IV. Fission of *as*-*tert.*-alkyl-*sec.*-alkylethylenes and isomerisation of *sec.*-alkylvinyl radicals of the general type, $CHR_2{\cdot}\dot{C}{:}CH_2$. I. N. NASAROV (Ber., 1937, **70**, [*B*], 606—617; 617—624; cf. A., 1936, 819).—III. The ethylenic hydrocarbons when distilled with 1 : 4-$C_{10}H_6Br{\cdot}SO_3H$ undergo fission at the point of union with the *tert.*-alkyl, giving ultimately a mixture of simpler olefines which are also formed by scission of the methyldi*tert.*-alkylcarbinols. The primary process, $CR_3{\cdot}C(:CH_2){\cdot}CR_3 \rightarrow \dot{C}R_3 + CR_3{\cdot}\dot{C}{:}CH_2$, is followed by stabilisation by respective loss and gain of H; union $2\dot{C}R_3 \rightarrow CR_3{\cdot}CR_3$ is not observed. If the olefine mol. contains two different *tert.*-alkyls fission occurs in both possible directions, the order of ease of fission being $Bu^\gamma > CMe_2Pr^\alpha$, $CMe_2Et > CMeEt_2 > CEt_3$, CMe_2Pr^β. CR_3 becomes stabilised to a di- or tri-substituted ethylene by loss of H. The radical $CR_3{\cdot}C{:}CH_2$ passes before hydrogenation from the vinyl to the allyl form, so that the ultimate products are mainly tetra-substituted ethylenes. The isomerisation of allyl radicals is fully discussed, and the conclusion is reached that the double linking tends to migrate to the most highly alkylated C. The requisite carbinols are dehydrated by slow distillation in presence of a trace of I. γγδεε-Pentamethylheptan-δ-ol yields *γγζζ-tetramethyl-ε-methyleneoctane*, b.p. 200—204°, transformed into $CMe_2{:}CHMe$, (?) βγ-dimethyl-Δ^α-pentene (I), and $CMe_2{:}CMeEt$. δδεζζ-Pentamethylnonan-ε-ol gives *δδηη-tetramethyl-ζ-methylenedecane*, b.p. 229—233°, whence $CMe_2{:}CHEt$ (*dimethylpropylcarbinyl chloride*, b.p. 110—113°) and $CMe_2{:}CMePr^\alpha$ (oxidised to $COMe_2$, COMePr, and a *liquid*, C_8H_{16}, b.p. 100—105°/22 mm.). ββγδδ-Pentamethylhexan-γ-ol affords *ββδδ-tetramethyl-γ-methylenehexane*, b.p. 176—181°, transformed into $CMe_2{:}CHMe$, $CMe_2{:}CMe_2$, (I), and $CMe_2{:}CMeEt$, which are also derived from ββγδδ-pentamethylhexan-γ-ol. ββγδ-Tetramethyl-δ-ethylhexan-γ-ol gives *ββδ-trimethyl-γ-methylene-δ-ethylhexane*, b.p. 198—203°, whence C_4H_8, $CMeEt{:}CHMe$, $CMe_2{:}CMe_2$, and $CMe_2{:}CEt_2$. Dehydration of ββγ-trimethyl-δδ-diethylhexan-γ-ol gives *iso*-C_5H_{10}, (?) $CMe_2{:}CMe_2$, and $CMeEt{:}CHEt$, and a *fraction*, C_9H_{18}, b.p. 130—140°. ββγδδ-Pentamethylheptan-γ-ol affords *ββδδ-tetramethyl-γ-methyleneheptane*, b.p. 195—199°, whence *iso*-C_4H_8, $CMe_2{:}CHEt$, $CMe_2{:}CMe_2$, and $CMe_2{:}CMePr$. ββγδδε-Hexamethylhexan-γ-ol yields *ββδδε-pentamethyl-γ-methylenehexane*, b.p. 195—200°, whence $CMe_2{:}CMe_2$, octene, and $CMe_2{:}CMePr^\beta$.

IV. Olefines $CR_3{\cdot}C(:CH_2){\cdot}CHR_2$ undergo fission to CR_3 which becomes stabilised by loss of H and $CHR_2{\cdot}C{:}CH_2$ which becomes isomerised to $\cdot CR_2{\cdot}CH{:}CH_2$ and thence to $CR_2{:}CH{\cdot}CH_2\cdot$, and then stabilised by addition of H, so that the final products are exclusively trisubstituted ethylenes. The isomerisation is entirely one-sided. The second step takes place according to the rule that the double linking tends to become displaced in the direction of the most highly alkylated atom. Dehydration of methyl*sec.*-alkyl-*tert.*-alkylcarbinols is readily effected by distillation with a trace of I, reaction commencing at about 110—120°. βγδδ-Tetramethylhexan-γ-ol gives γγε-*trimethyl-δ-methylenehexane*, b.p. 152—156°, whence *iso*-C_4H_8, $CMe_2{:}CHMe$, and $CMe_2{\cdot}CHEt$. ββγδ-Tetramethylhexan-γ-ol affords ββγ-*trimethyl-γ-methylenehexane*, b.p. 146—150°, which gives *iso*-C_4H_8, $CMe_2{:}CHMe$, and $CMe_2{:}CHEt$. ββδδ-*Trimethyl-γ-methyleneheptane*, b.p. 171—174°, from βγδδ-tetramethylheptan-γ-ol, yields $CMe_2{:}CHMe$, $CMe_2{:}CHEt$, and $CMePr^{\alpha}{:}CHMe$. ββγδ-Tetramethylheptan-γ-ol affords ββδ-*trimethyl-γ-methyleneheptane*, b.p. 169—174°, whence *iso*-C_4H_8, $CMe_2{:}CHMe$, $CMe_2{:}CHEt$, and $CMePr^{\alpha}{:}CHMe$. Dehydration of ββγ-trimethyl-δ-ethylhexan-γ-ol gives ββ-*dimethyl-γ-methylene-δ-ethylhexane*, b.p. 169—172°, whence *iso*-C_4H_8, $CMe_2{:}CHMe$, $CMe_2{:}CHEt$, and $CEt_2{:}CHMe$. ββγδε-Pentamethylhexan-γ-ol gives ββδε-*tetramethyl-γ-methylenehexane*, b.p. 167—171°, whence *iso*-C_4H_8, $CMe_2{:}CHMe$, $CMe_2{:}CMe_2$, and $CHMe{:}CMePr^{\beta}$. γε-*Dimethyl-δ-methylene-γ-ethylheptane*, b.p. 196—199°, from γδε-trimethyl-ε-ethylheptan-δ-ol, gives $CMe_2{:}CHMe$, $CMeEt{:}CHMe$, and $CMeEt{:}CHEt$. ββγ-Trimethyl-δ-propylheptan-γ-ol affords ββ-*dimethyl-γ-methylene-δ-n-propylheptane*, b.p. 205—207°, whence *iso*-C_4H_8 and $CHMe{:}CPr^{\alpha}_2$. For prep. of the above alcohols see this vol., 225. H. W.

Hydrogenation of acetylenic compounds. XXVII. Catalytic hydrogenation of βε-dimethyl-$\Delta^{\alpha\epsilon}$-hexadien-Δ^{γ}-ine. J. S. Salkind and Z. V. Smagina (J. Gen. Chem. Russ., 1937, 7, 470—475).—$(:C{\cdot}CMe{:}CH_2)_2$ and H_2 (Pd catalyst) yield βε-*dimethyl-*Δ^{α}-*hexene*, b.p. 111—113°, which is further hydrogenated to Bu^{β}_2 in presence of Pt catalyst. R. T.

Rate of hydration of acetylene.—See A., I, 313.

Technique of introducing radioactive halogens into organic molecules. N. E. Breshneva, S. Z. Roginski, and A. I. Schilinski (J. Phys. Chem. Russ., 1936, 8, 849—865).—EtBr was irradiated by neutrons, and the radioactive Br used for preparing radioactive $AlBr_3$. The latter rapidly and completely reacts with EtBr, $C_5H_{11}Br$, $(CH_2Br)_2$, CH_2PhBr, etc.; the exchange with PhBr, *p*-$C_6H_4Br_2$, and 1-$C_{10}H_7Br$ is slow. $AlBr_3$ reacts also with $CHCl_3$ and CCl_4 but not with EtI. Radioactive $AlCl_3$ does not exchange with bromides and iodides; AlI_3 reacts with both chlorides and bromides. J. J. B.

Photochemical formation of tetrachloroethane from *trans*-dichloroethylene and chlorine.—See A., I, 318.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. V. Comparison of the effect of oxygen with that of peroxide. Relation between the amount of oxygen present and the result of addition. Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1937, **12**, 138—144).—Previous results (this vol., 81) are confirmed and O_2 is shown to possess catalytic activity in the sense of, and >, the "peroxide effect." The activity is influenced by impurities in the allyl bromide. F. R. G.

Anomalous elimination of halogens from certain tri- and tetra-halides. A. A. Petrov and A. F. Saposhnikova (J. Gen. Chem. Russ., 1937, **7**, 476—484).—When heated with KOH in aq. EtOH, compounds, $CHMeX{\cdot}CMeX_2$, yield $(:CMeX)_2$, and of the type $(CMeX_2)_2$ yield $(CH_2{:}CX\cdot)_2$. Thus $CHMeBr{\cdot}CMeBr_2$ gives $(:CMeBr)_2$ (I), and $(\cdot CMeBr_2)_2$ gives $CH_2{:}CBr{\cdot}CBr{:}CH_2$. $CHMe{:}CMeCl$ (II) and Br yield β-*chloro-γγ-dibromobutane*, b.p. 66—66·5°/12 mm., which reacts with KOH to yield $CMeCl{:}CMeBr$ (III), from which β-*chloro-βγγ-tribromobutane*, m.p. 223—224°, is obtained, and this regenerates (III) when treated with EtOH–KOH. (II) and ClI in HCl afford ββ-*dichloro-γ-iodobutane*, b.p. 69·5°/11·5 mm., from which (II) is regenerated by heating with EtOH–KOH. $CHMe{:}CMeBr$ (IV) and ClI give a mixture of β-chloro-β- and -γ-bromo-γ-iodobutane, yielding (II) and (III) with EtOH–KOH. (IV) and BrI yield a mixture of ββ- and βγ-dibromo-γ-iodobutane, giving (I) and (IV) with EtOH–KOH. R. T

Synthesis of derivatives from αγ-dichloro-Δ^{β}-butene. Use of by-products from synthesis of chloroprene. A. L. Klebanski and K. K. Tschevuichalova (Sintet. Kautschuk, 1935, No. 6, 16—21).—αγ-Dichloro-Δ^{β}-butene (I) with EtOH–KOH affords *γ-chloro-α-ethoxy-*Δ^{β}-*butene*, b.p. 62—64°/40 mm., whereas aq. Na_2CO_3 affords *γ-chloro-*Δ^{β}-*buten-α-ol* (II), b.p. 92°/50 mm. (*xanthate*). (I) and (II), with aq. KOH, yield *di-(γ-chloro-*Δ^{β}-*butenyl) ether*, b.p. 142°/50 mm. (I) yields chloroprene when passed over various catalysts at high temp. Ch. Abs. (*r*)

Formation of chloronitroso-compounds from ethylenic hydrocarbons (C_6 to C_{11}). M. Tuot (Compt. rend., 1937, **204**, 697—699).—Hydrocarbons of type $CRR'{:}CHR''$ or $CRR'{:}CR''R'''$ react readily, those of type $CHR{:}CHR'$ with difficulty, with NOCl (from $C_5H_{11}{\cdot}O{\cdot}NO$, or, better, from $SOCl_2 + N_2O_3$ mixed with the hydrocarbon at —5°) to form chloronitrosoparaffins (or chloro-oximes). The following *compounds* are prepared: from $CHMe{:}CMeEt$, $C_6H_{12}ONCl$, m.p. 66°; from $CMe_2{:}CHPr^{\alpha}$, $C_7H_{14}ONCl$, m.p. 67°; from $CHMe{:}CEt_2$, $C_7H_{14}ONCl$, m.p. 86°; from $CMe_2{:}CHBu^{\beta}$, $C_8H_{16}ONCl$, m.p. 123°; from $CMeEt{:}CHBu^{\beta}$, $C_9H_{18}ONCl$, m.p. 113°; from $CMe_2{:}CMeBu^{\beta}$, $C_9H_{18}ONCl$, m.p. 158°; and from $CMeBu^{\beta}{:}CHBu^{\beta}$, $C_{11}H_{22}ONCl$, m.p. 109°. E. W. W.

Nitration of paraffins by nitrogen peroxide. T. Urbanski and M. Slon (Compt. rend., 1937, **204**, 870—871; cf. A., 1936, 1485).—*n*-C_5H_{12} with N_2O_4 at 200° affords *mono-*, b.p. 164—165°/750·3 mm. (60%), and *di-nitropentane* (40%). *n*-C_6H_{14} and *n*-C_7H_{16} similarly give $(NO_2)_1$-, b.p. 185°/780·3 mm.

and b.p. 199—200°/750·3 mm., and $(NO_2)_2$-derivatives, respectively. *n*-C_8H_{18} and *n*-C_9H_{20} afford mixtures which decompose when distilled. J. L. D.

Aliphatic nitro-compounds. IV. Reactions of nitromethane halides with metal-organic compounds. N. N. Melnikov (J. Gen. Chem. Russ., 1937, **7**, 456—460).—The following reactions are described: $CX_3{\cdot}NO_2$ (I) + 4MgPhX → OR·MgX + Ph_2 + MgO,MgX + $CX_3{\cdot}NPh{\cdot}MgX$; (I) + $3HgEt_2$ → $CEt_3{\cdot}NO_2$ + 3HgEtX (II); $3C_4H_{10}$ + 6(II) + N_2 + $2CO_2$ ← 2(I) + $6HgEt_2$ → $3C_4H_{10}$ + 6(II) + 2CO + 2NO; PPh_3X_2 + N_2 + $2CO_2$ ← 2(I) + $3PPh_3$ → $3PPh_3X_2$ + 2NO + 2CO (X = Cl, Br). R. T.

Biochemical hydrogenations. IV. Hydrogenation of crotyl alcohol by *coli* bacteria. F. G. Fischer and W. Robertson (Annalen, 1937, **529**, 84—87; cf. A., 1936, 588).—Crotyl alcohol in concn. 1 : 1000 does not appreciably restrict the growth of the bacteria or fermentation; its partial reduction is established. Indecisive results are obtained with CHPh:CH·CH_2·OH. H. W.

Synthesis of tertiary alcohols $CR_3{\cdot}CMe(OH){\cdot}CHR_2$ and $CR_3{\cdot}CMe(OH){\cdot}CR_2$. Action of magnesium methyl bromide on branched ketones. I. N. Nasarov (Ber., 1937, **70**, [*B*], 599—605).—Ketones $CR_3{\cdot}CO{\cdot}CHR_2$ and $CO(CR_3)_2$ are converted by MgMeBr into the corresponding *tert.*-alcohols without formation of by-products. The difficulty of the action increases when Me (= R) is replaced by Et and particularly by Pr^{β}, but is not greatly altered when Pr^{α} replaces Me; it also increases on passage from $CR_3{\cdot}CO{\cdot}CHR_2$ to $CO(CR_3)_2$. Very little *tert.*-alcohol results from the ketone and MgEtBr or $MgPr^{\alpha}Br$, the main change being reduction to the *sec.*-alcohol. Methylethylpinacolin and MgMeBr afford ββγδ-*tetramethylhexan-γ-ol*, b.p. 190—193°. The following alcohols are obtained analogously: βγδδ-*tetramethylhexan-γ-ol*, b.p. 197—199°; ββγ-*trimethyl-δ-ethylhexan-γ-ol*, b.p. 208—211°; γδε-*trimethyl-γ-ethylheptan-δ-ol*, b.p. 235—238°; ββγ-*trimethyl-δ-propylheptan-γ-ol*, b.p. 234—237·5°; ββγδ-*tetramethylheptan-γ-ol*, b.p. 212—215°; βγδδ-*tetramethylheptan-γ-ol*, b.p. 215—217°; ββγδε-*pentamethylhexan-γ-ol*, b.p. 207—210°; ββγδδ-*pentamethylhexan-γ-ol*, b.p. 219—222°; ββγδ-*tetramethyl-δ-ethylhexan-γ-ol*, b.p. 237—240°; γγδεε-*pentamethylheptan-γ-ol*, b.p. 243—246°; ββγ-*trimethyl-δδ-diethylhexan-γ-ol*, b.p. 252—256°; δδεζζ-*pentamethylnonan-ε-ol*, b.p. 266—269°; ββγδδ-*pentamethylheptan-γ-ol*, b.p. 233—235°; ββγδδε-*hexamethylhexan-γ-ol*, b.p. 235—238°. H. W.

Sulphuric [acid] dehydration of divinyl glycol. Hydrobenzoin type of rearrangement with migration of the vinyl group. M. Tiffeneau and P. Weill (Compt. rend., 1937, **204**, 590—592).—[CH_2:CH·CH(OH)·]$_2$ with 50% H_2SO_4 at 100—120° gives a 40—50% yield of a mixture, b.p. 140—150°, containing mainly *α-vinylcrotonaldehyde*, reduced (Raney Ni) with H_2 to give *α-ethylcrotonaldehyde* (*semicarbazone*, m.p. 210°) (synthesised from $Pr^{\alpha}CHO$ and MeCHO and dehydration of the aldol), and with $3H_2$ to give $CHEt_2{\cdot}CH_2{\cdot}OH$. No trace of Δ^1-*cyclo*pentene-1-aldehyde (Urion, A., 1934, 389) was detected. J. W. B.

Catalytic and acid dehydration of divinyl glycol. E. Urion and E. Baum (Compt. rend., 1937, **204**, 595—597).—α-Vinylcrotonaldehyde (I) (preceding abstract) is not converted into Δ^1-*cyclo*pentene-1-aldehyde (II) by passage over Al_2O_3 at 320°. (I) is also obtained in very small yield from divinyl glycol (III) and boiling 2% H_2SO_4. Temp. is the main factor which determines the formation of (I) (<200°) or (II) (>200°) by dehydration of (III). Thus (III) and 8% H_2SO_4 at 200—210° give some (II). No dehydration of (III) could be effected with Al_2O_3 at <200°/7—8 mm. J. W. B.

Action of formic acid on tetraethylbutinediol. V. N. Krestinski and N. I. Summ (J. Gen. Chem. Russ., 1937, **7**, 440—455).—(:C·$CEt_2{\cdot}OH)_2$ and HCO_2H or 20% H_2SO_4 at 80° yield *γζ-diethyl-*$\Delta^{\beta\zeta}$*-octadien-*Δ^{δ}*-ine*, b.p. 169—171°, which yields AcOH, $EtCO_2H$, OH·CHMe·CEt(OH)·CO_2H, and OH·CEtAc·CO_2H with $KMnO_4$, *γζ-diethyl-*Δ^{δ}*-octene* (I), b.p. 198° (*dibromide*, b.p. 114—115°/4 mm.), with H_2 in presence of Pd, and γζ-diethyloctane in presence of Pt catalyst. (I) is oxidised by $KMnO_4$ to AcOH, $EtCO_2H$, and $CHEt_2{\cdot}CO_2H$. R. T.

Derivatives of the oxidation products of glycerol. H. P. den Otter (Rec. trav. chim., 1937, **56**, 474—491).—Glycerol oxidised with H_2O_2 and $FeSO_4$ yields glyceraldehyde, OH·CH_2·CO·CHO (I), HCO_2H, and AcCHO; with NaOCl or $Ca(OCl)_2$, CH_2O and (probably) β-acrose are formed, whilst with Br and Na_2CO_3, dihydroxyacetone (II) is obtained. From glyoxal, the following are prepared: 3-*nitro-*, m.p. 292°, 5-*chloro*-2-*nitro-*, m.p. 319—320°, 5-*bromo*-2-*nitro-*, m.p. 320—325° (decomp.), and 4 : 6-*dinitro*-3-*ethoxyphenyl-*, m.p. 330° (decomp.), o-, m.p. 105—106°, m-, m.p. 125—126°, p-*tolyl-*, m.p. 224° (decomp.), α-, m.p. 211°, and β-*naphthyl-osazone*, m.p. 252°. *Dihydroxyacetone*-5-*chloro*-2-*nitro-*, m.p. 136°, 5-*bromo*-2-*nitro-*, m.p. 155—156°, and 4 : 6-*dinitro*-3-*ethoxyphenylhydrazone*, m.p. 124—126°, and -2-*nitro-*, m.p. 210°, -3-*nitro-*, m.p. 192°, -5-*chloro*-2-*nitro-*, m.p. 244°, -5-*bromo*-2-*nitro-*, m.p. 256—258° (decomp.), -4 : 6-*dinitro*-3-*ethoxyphenyl-*, m.p. 296°, and *-benzoyl-osazone*, m.p. 220°, are described. Oxidation [$Cu(OAc)_2$] of (II) affords (I) which yields the following derivatives which cannot be formed from (II) and the appropriate hydrazine: *dihydroxyacetone-phenylmethyl-*, m.p. 145°, -o-, m.p. 145—148°, -m-, m.p. 156°, and -p-*tolyl-*, m.p. 167°, *-diphenyl-*, m.p. 241°, and *-phenylbenzyl-osazone*, m.p. 194°. The phenylosazone of (II) with PhCHO, HCl, or glucose does not yield (I). J. D. R.

Preparation of synthetic ethers from α-chloroethers. H. I. Waterman, W. J. C. de Kok, J. J. Leendertse, and W. H. Schoenmaker (Rec. trav. chim., 1937, **56**, 437—441).—The reaction CHRCl·OR′ + MgR″X → CHRR″·OR′ has been applied to the synthesis of OEt·CHMeEt, OEt·CHMe·C_5H_{11}-*n*, and $CH_2Ph{\cdot}O{\cdot}CH_2Bu^{\beta}$. Physical consts. are recorded. J. D. R.

Chlorination of propylene oxide. A. F. Dobrianski, M. I. Davidova, and Z. T. Pankina (J.

Gen. Chem. Russ., 1937, **7**, 291—297).—The chief product of chlorination at 0° is $COMe\cdot CH_2Cl$, together with other compounds, of which $OH\cdot CHMe\cdot CH_2Cl$ is identified. R. T.

Preparation of divinyl ether. W. A. Lott, F. A. Smith, and W. G. Christiansen (J. Amer. Pharm. Assoc., 1937, **26**, 203—208).—The ether is obtained in yields of 21—36% from $(CH_2Cl\cdot CH_2)_2O$ with solutions of KOH or, *e.g.*, Na *tert.*-hexoxide in higher alcohols (*e.g.*, octyl). F. O. H.

Syntheses of glycerides with the aid of triphenylmethyl compounds. III. Triglycerides. P. E. Verkade, J. van der Lee, and (Frl.) W. Meerburg (Rec. trav. chim., 1937, **56**, 365—374).—γ-Triphenylmethylglyceryl α-stearate (A., 1936, 704) with myristyl chloride (I) in dry quinoline–$CHCl_3$ at room temp. affords *γ-triphenylmethylglyceryl β-myristate α-stearate*, m.p. 43·5—44°, which with HCl (gas) in cold Et_2O affords *glyceryl γ-myristate α-stearate*, m.p. 66—66·5°. γ-Triphenylmethlyglyceryl α-palmitate likewise affords *γ-triphenylmethylglyceryl β-myristate α-palmitate*, m.p. 27—28°, whence *glyceryl γ-myristate α-palmitate* (II), m.p. 63·5—64°. Glyceryl γ-palmitate α-stearate similarly affords *glyceryl β-myristate γ-palmitate α-stearate*, m.p. 59·5—60° (labile form, m.p. 55—56°). Similarly, glyceryl γ-myristate α-stearate gives *glyceryl γ-myristate β-palmitate α-stearate*, m.p. 58·5—59°, and (II) gives *glyceryl γ-myristate α-palmitate β-stearate*, m.p. 58·5—59°. J. L. D.

Thioglycerols. H. Rheinboldt and C. Tetsch (Ber., 1937, **70**, [*B*], 675—680).—Gradual addition of $OH\cdot CH(CH_2Cl)_2$ to a solution of NaHS in abs. EtOH at 65° gives *β-hydroxy-αγ-dithiolpropane* (αγ-dithioglycerol), b.p. 94°/12 mm. (*Hg*, m.p. 185°, and *Pb*, decomp. 175—180° after darkening at 130°, compounds). Analogously $CHBr(CH_2Br)_2$ affords *αβγ-trithiolpropane* (trithioglycerol), b.p. 115—120°/12 mm., insol. in H_2O, sol. in Et_2O; it gives a *Hg* compound, $C_6H_{10}S_6Hg_3$, decomp. about 170°, *Pb* derivative, incipient decomp. 130°, *Ag* compound, gradual decomp. >150°; it is transformed by Me_2SO_4 and NaOH into *αβγ-trimethylthiolpropane*, b.p. 147°/15 mm., oxidised by H_2O_2 in AcOH to the corresponding *trisulphone*, m.p. 206°. *Trithioglyceryl tripalmitate*, $C_3H_5(S\cdot CO\cdot C_{15}H_{31})_3$, has m.p. 71°. H. W.

Ethyl ethylsulphenate. A. Meuwsen and H. Gebhardt (Ber., 1937, **70**, [*B*], 792—796).—Interaction of EtOCl with NaSEt in Et_2O affords Et_2S_2. SEt·SCN and NaOEt in Et_2O yield *Et ethylsulphenate* (I), SEt·OEt, b.p. 38·2—38·5°/50 mm., 107·8—108·5°/724 mm., which is not readily autoxidised, does not reduce SeO_2 to Se, and does not give well-defined products with NO_2 or $KMnO_4$ in $COMe_2$. It is smoothly oxidised by EtOCl in Et_2O to Et ethylsulphinate (II), b.p. 62—63°/15—16 mm.; analogously $S(OEt)_2$ affords $SO(OEt)_2$. Ozonisation of (I) in CCl_4 at about −20° gives (II), whereas at room temp. Et ethylsulphonate is produced; Et_2S and Et_2SO are similarly oxidised to Et_2SO_2. Hydrolysis of (I) by $Ba(OH)_2$–MeOH leads to *Ba ethylsulphinate*. Mg ethylsulphinate and $HgCl_2$ afford the *compound* $(EtSO_2)_2Hg,HgCl_2$. H. W.

Action of the sulphonyl group. F. Arndt (J. Amer. Chem. Soc., 1937, **59**, 759—760).—SO_3H promotes enolisation by diminishing the prototropic expenditure of work necessary; CO_2H promotes it directly by increasing the electromeric effect of the mol. The difference in degree of enolisation caused by these groups is thus due to a difference in the nature of the mechanism (cf. Kohler *et al.*, this vol., 23). R. S. C.

Reaction between sulphur dioxide and olefines. V. Structure of the polysulphones from olefines of the type $CHR{:}CH_2$. F. J. Glavis, L. L. Ryden, and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 707—711; cf. A., 1936, 1487).—By further examples (cf. A., 1935, 1349) it is shown that olefines, $CHR{:}CH_2$, condense with SO_2 to head-head-tail-tail polymeric sulphones (*A*), . . . $CH_2\cdot CHR\cdot SO_2\cdot[CHR\cdot CH_2\cdot SO_2\cdot CH_2\cdot CHR\cdot SO_2]_x\cdot CHR\cdot CH_2\cdot SO_2\cdot$ . . . Δ$^\alpha$-Pentenepolysulphone (*A*; R = Pr$^\alpha$) with hot 20% NaOH gives Pr$^\alpha$CHO and *Na α-methylsulphonyl-*n*-pentane-β-sulphinate*, $+H_2O$, oxidised by H_2O_2 to the corresponding *sulphonate* (I), which gives the *sulphonyl chloride* (II), m.p. 64—65°. Δ$^\alpha$-Pentene and HOCl give *α-chloropentan-β-ol*, b.p. 68—75°/30 mm., and thence successively *α-methylthiolpentan-β-ol* (by NaSMe), b.p. 90°/18 mm., *β-chloro-α-methylthiolpentane* (by $SOCl_2$), b.p. 84—86°/20 mm., *Na α-methylthiolpentane-β-sulphonate* (by $Na_2S_2O_3$), (I) (by $KMnO_4$), and (II). The polysulphones from C_3H_6, Δ$^\alpha$-C_5H_{10}, -C_8H_{16}, -C_9H_{18}, and *styrenepolysulphone* (*A*; R = Ph), m.p. 185—190°, give 2 : 6-disubstituted 1 : 4-*dithian* 1 : 4-*bisdioxides*, $SO_2<\begin{matrix}CHR\cdot CH_2\\CHR\cdot CH_2\end{matrix}>SO_2$, in which R = Me, m.p. 334°, Pr$^\alpha$, m.p. 257°, *n*-C_6H_{14}, m.p. 265°, *n*-C_7H_{16}, m.p. 260—261°, and Ph, m.p. 280°. The original olefine (C_3H_6 etc.), when treated first with S_2Cl_2 [gives probably $S(CH_2\cdot CHRCl)_2$] and then with Na_2S in dry EtOH, gives 2 : 6-*di-methyl-*, b.p. 85—87°/12 mm., -*n-propyl-*, b.p. 145—155°/20 mm., and -*phenyl*-1 : 4-*dithian*, b.p. 190—195°/30 mm., oxidised by H_2O_2 to the bisdioxides. R. S. C.

Reactions of mercury diethyl with certain acid chlorides. N. N. Melnikov and M. S. Rokitskaja (J. Gen. Chem. Russ., 1937, **7**, 464—466).—$HgEt_2$ reacts with R·COCl or OR′·COCl to yield respectively COEtR or $EtCO_2R'$, with HgEtCl (R = Me, Bu$^\beta$, Ph; R′ = Me, Et). R. T.

Electrolytic dissociation processes. II. Friedel–Crafts reaction.—See A., I, 320.

Oxidation of acetic, propionic, butyric, and *iso*valeric acids by molecular oxygen with ultraviolet light.—See A., I, 318.

Electrolysis of deutero-fatty acids. I. Electrolysis of deuteroacetic acid. P. Hölemann and K. Clusius (Z. physikal. Chem., 1937, **B**, **35**, 261—269).—The electrolysis of $CD_3\cdot CO_2D$ and $CD_3\cdot CO_2Na$ in H_2O and of AcOH in D_2O has been investigated. Only with the solutions in H_2O does the C_2H_6 given off contain D, which shows that there is no interchange of D and H between the solvent and the Me formed as intermediate product in the production of C_2H_6. A

micro-balance for determining the *d* of C_2H_6 is described. R. C.

Electrolysis of fatty acids containing deuterium. II. Mechanism of the formation of ethylene during the electrolysis of propionic acid. P. HÖLEMANN and K. CLUSIUS (Ber., 1937, **70**, [*B*], 819—827).—Examination of the products obtained by the electrolysis of $CD_3{\cdot}CH_2{\cdot}CO_2H$ and $CD_2Me{\cdot}CO_2D$ shows that in the production of C_2H_4 by the electrolysis of $EtCO_2H$ the primary dehydrogenation of Et occurs by loss of H from Me. Et is regarded as a semi-prepared C_2H_4 in which a marked strengthening of the C–C linking has occurred with consequent considerable weakening of the C–H linking. The subsidiary production of C_2H_6 is ascribed to disproportionation of C_2H_4; this is justified from the viewpoint of energy. *ββ-Trideuteropropionic acid* is obtained by the electrolysis of a solution of $CD_3{\cdot}CO_2K$ and $CO_2K{\cdot}CH_2{\cdot}CO_2Et$ in H_2O as catholyte and 25% K_2CO_3 as anolyte with Pt electrodes in a U-tube provided with a glass-wool plug; a stream of CO_2 is passed through the catholyte. The ester mixture is separated by distillation under diminished pressure at 0° and the appropriate fraction is hydrolysed. *Trideuteroacetic deuteracid* is prepared by heating $CHMe(CO_2H)_2$ with 99·21% D_2O at 55°. H. W.

Influence of *cis-trans*-isomerism on selective hydrogenation. V. P. GOLENDEEV (J. Gen. Chem. Russ., 1937, **7**, 317—327).—The allyl double linkings of allyl oleate (I) or elaidate (II) are hydrogenated (160°; Pd–$BaSO_4$ catalyst) before those of the acids, and of (II) before those of (I). The velocity of hydrogenation of the acid double linking of (I) > of (II). R. T.

Transposition of the double linking in Δ$^{\epsilon}$- and Δ$^{\theta}$-oleic acid. I. I. VANIN and A. A. TSCHERNOJAROVA (Ber., 1937, **70**, [*B*], 624—628).—A fuller account of work already reported (A., 1936, 705). H. W.

Synthesis of unsaturated fatty acids. II. Linoleic and λ-*n*-amyl-Δ$^{\theta\kappa}$-tridecadienoic acids. C. R. NOLLER and M. D. GIRVIN (J. Amer. Chem. Soc., 1937, **59**, 606—608; cf. A., 1934, 991).—Δ$^{\epsilon}$-Octen-β-ol (from $CH_2{:}CH{\cdot}CHO$ and $C_5H_{10}{\cdot}MgBr$), b.p. 78—81°/20 mm., and PBr_3 give a mixed *bromide*, b.p. 87—89°/20 mm., the Grignard reagent from which with θ-chloro-αβ-dibromo-α-methoxynonane gives a product, converted by Zn etc. into impure Δ$^{\theta\lambda}$-*heptadecadienyl chloride*, b.p. 165—171°/6 mm., which with KCN gives the impure *cyanide*, b.p. 185—187°/3 mm., hydrolysed to an oily acid. This acid gives no oleic acid tetrabromide before or after elaidinisation, but yields α- and β-sativic acid and thus contains some oleic acid; the presence of >30% of κ-vinyl-Δ$^{\theta}$-hexadecenoic acid is indicated by formation of 0·16 mol. of CH_2O by O_3 (pure undecenoic acid gives only 0·44 mol.). R. S. C.

Naturally occurring linoleic acid in cottonseed and soya-bean oils and the regenerated linoleic acid from α-linoleic acid tetrabromide of these oils. D. M. BIROSEL (J. Amer. Chem. Soc., 1937, **59**, 689—692).—The free fatty acids of soya-bean and cottonseed oils with $KMnO_4$ give only α- (I) and β-sativic acid (II) and with Br only α-linoleic acid tetrabromide (III); the α-linoleic acid regenerated from (III) yields only (III) with Br, and only (I) and (II) with $KMnO_4$. R. S. C.

Configurative relationship of α-hydroxy-*n*-valeric and α-hydroxy*iso*valeric acids. P. D. BARTLETT, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1837, **118**, 503—511).—iso*Propylcrotylcarbinol*, b.p. 51—54°/15 mm., prepared from $CHMe{:}CH{\cdot}CHO$ and Pr$^{\beta}$Br, yields the (+)-*carbinol* (I), same b.p., $[\alpha]_D^{25}$ +19·36° [*H phthalate*, $[\alpha]_D^{25}$ +16·8° in EtOH (*strychnine* salt, sets at −10°)], which is ozonised to (−)-α-*hydroxy*iso*valeraldehyde* (II), $[\alpha]_D^{25}$ −5·4° in Et_2O; this could not be satisfactorily converted into the acid. Reduction (Na–Hg) of (II) gives (+)-β-*methylbutane-γδ-diol*, b.p. 103°/12 mm., $[\alpha]_D^{25}$ +3·9° in Et_2O, which could not be catalytically reduced. (I) is hydrogenated (Adams) to (+)-*propyl*iso*propylcarbinol* (III), b.p. 52°/12 mm., $[\alpha]_D^{25}$ +15·03°. (−)-iso*Propylcrotylcarbinol* (IV), $[\alpha]_D^{25}$ −11·4°, yields an *Ac* derivative, b.p. 86—87°/46 mm., $[\alpha]_D^{25}$ +21·3°, which with $KMnO_4$–$COMe_2$ forms (+)-α-*acetoxy*iso*valeric acid* (V), b.p. 95—97°/3 mm., $[\alpha]_D^{25}$ +8·62° (*Me* ester, b.p. 50°/1 mm., $[\alpha]_D^{25}$ +9·25°). (+)-α-*Hydroxy*iso*valeric acid*, from *d*-valine or from α-bromo-*iso*valeric acid, has a small + rotation, dependent on concn., which changes to a − rotation in the *Na* salt; the *Et* ester, b.p. 112—114°, has $[\alpha]_D^{25}$ +0·30° [*Ac* derivative (VI), b.p. 80°/10 mm., $[\alpha]_D^{27}$ −9·83°].

(−)-α-Hydroxy-*n*-valeric acid (VII) has previously been correlated with (+)-$CHMePr^{\alpha}{\cdot}OH$, and thus with (III) and with (I); from the relationships of (IV), (V), and (VI), it follows that (−)-α-hydroxy*iso*valeric acid is configuratively related to (VII). E. W. W.

Configurative relationship of α-hydroxy-*n*-hexoic and α-hydroxy*iso*hexoic acids. P. D. BARTLETT, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1937, **118**, 513—517).—(−)-iso*Butylcrotylcarbinol* (I), $[\alpha]_D$ −1·46° (resolution through the *strychnine* salt of the *H phthalate*, which when heated gives a *substance*, b.p. 30°/12 mm., probably ζ-methyl-Δ$^{\beta\delta}$-heptadiene), is hydrogenated to (+)-*propyl*iso*butylcarbinol* (II), b.p. 72°/15 mm., α +3·00°, and is ozonised to (+)-α-*hydroxy*iso*hexaldehyde*, b.p. 79°/18 mm., $[\alpha]_D^{25}$ +6·0°. In C_5H_5N with Ac_2O, (I) gives its *Ac* derivative, b.p. 88—90°/30 mm., $[\alpha]_D^{25}$ +13·7°, which with $KMnO_4$–$COMe_2$ yields (+)-α-*acetoxy*iso-*hexoic acid*, b.p. 127°/5 mm., $[\alpha]_D^{25}$ +9·91° [*Me* ester (III), b.p. 68°/5 mm., $[\alpha]_D^{27}$ +10·5°]. (−)-α-*Hydroxy*-iso*hexoic acid*, $[\alpha]_D^{25}$ −11·8° (from *l*-leucine), is converted into the *Et* ester, b.p. 118°/90 mm., $[\alpha]_D^{25}$ −7·06° [*Ac* derivative (IV), b.p. 74°, $[\alpha]_D^{27}$ −34·8°]. (−)-α-Hydroxy-*n*-hexoic acid (V) has already been correlated with (+)-methyl-*n*-butylcarbinol, and thus with (II) and (I); from the above relationships, and the rotations of (III) and (IV), it is seen that (V) is configuratively related to (+)-α-hydroxy*iso*hexoic acid. As (V) and (−)-α-hydroxy-*n*-valeric acid have the same configuration, α-hydroxy-*iso*valeric and -*iso*hexoic acids of the same configuration have opposite rotations; thus the effect of Pr$^{\beta}$ on the rotation of OH-acids varies with its distance from the asymmetric C-atom. *iso*Butylvinylcarbinol could not be resolved. E. W. W.

Catalysis of maleic–fumaric acid isomerisation by hydrogen ions. C. Horrex (Trans. Faraday Soc., 1937, **33**, 570—571).—Fumaric acid obtained by heating maleic acid with 2*N*-DCl in 99·5% D_2O and recrystallising twice from a large excess of H_2O contains no D. Since, if the isomerisation with acids proceeds by way of the addition of H· or HX at the double linking, the added H atom cannot be the one eliminated, the above observation indicates that the geometrical inversion does not proceed by this mechanism. F. L. U.

Catalytic hydrogenation and esterification of C_4-saccharolactones and the hydrogenation of butyl erythronate. J. W. E. Glattfeld and (Miss) A. M. Stack (J. Amer. Chem. Soc., 1937, **59**, 753—759).—Na βγ-dihydroxybutyrate and AcCl at 50—85° give 57% of β-acetoxy-γ-butyrolactone (I), b.p. 119—121°/4 mm., and 9·6% of (?) *trans*-γ-acetylcrotonic acid, m.p. 99—102°. Hydrogenation of β-hydroxy-γ-butyrolactone (II) at ≯120 atm. in presence of PtO_2, Cu–Cr, Pd, Cu–Ba–Cr, Cu–Cr (57 atm.), or Raney Ni gives γ-butyrolactone, also obtained from (I) by H_2–PtO_2 at 129 atm., but similar reduction of α-hydroxy-γ-butyrolactone (III), βγ-dihydroxybutyramide, erythronolactone, and erythronamide gives indefinite results. Hydrogenation of (II) and (III) in H_2O occurred at 2—3 atm. (PtO_2), but the products were not isolated. Bu erythronate in 95% EtOH with H_2–PtO_2 at 2—3 or 95 atm. gives good yields of erythritol. Esters of the dihydroxy-acids could not be obtained. (II) with H_2SO_4–BuOH gives *Bu* β-*hydroxyisocrotonate*, b.p. 174—181°/2 mm., with EtOH–H_2SO_4–anhyd. $CaSO_4$ gives γ-crotonolactone, and with HCl–EtOH gives *Et* γ-*chloro*-β-*hydroxybutyrate*, b.p. 92—95°/4 mm. (III) gives similarly *Et* γ-*chloro*-α-*hydroxybutyrate*, b.p. 92—95°/1—5 mm. R. S. C.

Duality of oxidised forms and polarisation of vitamin-*C*.—See A., III, 232.

Determination of ascorbic acid.—See A., III, 233.

Stabilisation of ascorbic acid by metaphosphoric acid. K. Hinsberg (Biochem. Z., 1937, **290**, 125—128).—A solution of ascorbic acid in 50% HPO_3 retains its titre almost unchanged for days whereas when treated with $CCl_3{\cdot}CO_2H$ it is rapidly destroyed. P. W. C.

Gluco-ascorbic acid. W. N. Haworth, E. L. Hirst, and J. K. N. Jones (J.C.S., 1937, 549—556).—*d*-Gluco-ascorbic acid (improved prep.) [*phenylosazone* (?), m.p. 215°] with CH_2N_2 in MeOH–Et_2O affords 3-*methyl*-d-*gluco-ascorbic* acid, m.p. 142°, $[\alpha]_D^{20}$ −25° in H_2O, further converted by CH_2N_2 in MeOH into 2 : 3-*dimethyl*-d-*gluco-ascorbic acid* (I), m.p. 94°, $[\alpha]_D^{20}$ −22° in H_2O, −7° in MeOH, which, after repeated methylation (MeI–Ag_2O) in anhyd. $COMe_2$, yields *trimethylisopropylidenegluco-ascorbic acid*, b.p. 150° (bath)/0·04 mm., $[\alpha]_D^{21}$ −1·6° in MeOH. Hydrolysis of this followed by repeated methylation (MeI–Ag_2O) affords 2 : 3 : 5 : 6 : 7-*pentamethylgluco-ascorbic acid*, m.p. 80°, $[\alpha]_D^{20}$ −5° in MeOH, +21° in CCl_4, oxidised (O_3 in CCl_4) to 3 : 4 : 5-*trimethyl*-d-*arabonic acid*, m.p. 67°, $[\alpha]_D^{19}$ +5° in MeOH {*Me* ester, b.p. 110° (bath)/0·03 mm., $[\alpha]_{5461}^{18}$ −17·5° in MeOH; *amide*, m.p. 51°, $[\alpha]_{5461}^{17}$ −30° in H_2O}, which with MeI–MeOH–Ag_2O affords *Me* 2 : 3 : 4 : 5-*tetramethyl*-d-*arabonate*, b.p. 100° (bath)/0·1 mm. (*amide*, m.p. 101°, $[\alpha]_D^{20}$ +33° in MeOH, identical with 2 : 3 : 4 : 5-*tetramethyl*-l-*arabonamide*, m.p. 101°, $[\alpha]_D^{17}$ +34·0° in MeOH, from Ca *l*-arabonate with Me_2SO_4–NaOH and MeI–Ag_2O). (I) with $Ba(OH)_2$ affords iso*dimethylgluco-ascorbic acid*, b.p. 230°/0·01 mm., $[\alpha]_D^{20}$ ±0° in H_2O, converted by H_2SO_4–$COMe_2$ into (I), or by HCl–MeOH into (I) and 2-*monomethylgluco-ascorbic acid*. J. D. R.

Semi-micro-determination of hexuronic acids. W. Voss and J. Pfirschke (Ber., 1937, **70**, [*B*], 631—634).—The substance (= about 50 mg. of lactone) is weighed into a flask containing a glass bead and two Pt tetrahedra. 10 c.c. of 20*M*-$ZnCl_2$ and about 0·5 g. of melted hard paraffin are added and, after the latter has solidified, the flask is connected with the condenser and gas burette. After 1 hr. the Hg level, barometric height, and temp. are determined. The liquid is heated to gentle boiling during 4 hr., after which it is allowed to cool until the paraffin has solidified (thus preventing back-diffusion of CO_2). After 1 hr. the above observations are repeated. A blank experiment is unnecessary. After addition of a const. correction dependent on the particular apparatus used, the variation between observed and calc. vals. is ≯0·2%. H. W.

Effect of iodine on rates of decomposition of formaldehyde, acetaldehyde, and propaldehyde.—See A., I, 314.

Formaldehyde from percarbonate.—See A., I, 321.

Kinetics of polymeric aldehydes. III. Physical influences on the rate of dissolution of polyoxymethylenes. J. Löbering (Ber., 1937, **70**, [*B*], 665—668; cf. A., 1936, 1232, 1362).—The rate of dissolution of polyoxymethylenes (I) is not affected by the rate of stirring of the mixtures; hence diffusion is not concerned in the process and degradation does not occur in the solid crystal. This view is strengthened by the observation that the rate of dissolution is independent of the size of the particles. A definite solubility product must be assigned to (I), the long chains of which are depolymerised in solution. The determining factor is the rupture of C·O·C linkings in solution which is catalytically accelerated by H· and OH'. H. W.

Absorbent for determination of acetaldehyde. J. V. Rakitin (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 445—448).—The best conditions and a suitable apparatus for the most complete absorption of MeCHO in $NaHSO_3$ and for its titration are outlined. P. W. C.

Production of nonaldehyde and nonyl alcohol. R. Shagalova (Maslob. Shir. Delo, 1935, **11**, 452—453).—An improved prep. from undecenoic acid is described. Ch. Abs. (*r*)

Production of decaldehyde. O. Osipova (Maslob. Shir. Delo, 1935, **11**, 378—379).—A 70—75% yield is obtained by passing the mixed vapours of *n*-decoic and formic acids over MnO at 350—375°. Ch. Abs (*r*)

Free radicals and atoms in primary photochemical processes. Dissociation of aliphatic ketones; the acetyl radical. H. H. Glazebrook and T. G. Pearson (J.C.S., 1937, 567—571; cf. A., 1935, 1211).—The relative quantities of radicals formed by the photolysis of $COMe_2$, COMeEt, $COMePr^{\alpha}$, $COMePr^{\beta}$, $COMeBu^{\alpha}$, $COPr^{\alpha}_2$, and $COPr^{\beta}_2$ have been measured by the relative rates of interaction with Te. The radicals from the photolysis of $COBu^{\gamma}_2$ could not be identified, but Me, Et, and Pr were absent. The products of photolysis of $COMe_2$ by ultra-violet light are Me and COMe. COMe radicals rapidly combine to Ac_2, have a life of $<10^{-4}$ sec., are quantitatively decomposed by SiO_2 at 60°, and are removed at room temp., probably by dissociation to Me and CO. J. D. R.

Determination of acetone. C. O. Haughton (Ind. Eng. Chem. [Anal.], 1937, **9**, 167—168).—Messinger's CHI_3 method gives 102·5% $COMe_2$ with pure samples (the products containing about 0·6% of HCO_2H). The oxime reaction of Marasco (indicator, Me-orange–xylene-cyanol) is 97·1% complete. A. L.

Alkylation of ketones with sodamide. Propylation of ketones. I. N. Nasarov (Ber., 1937, **70**, [*B*], 594—598).—The introduction of Me, Et, Pr^{α}, and Pr^{β} occurs in order of increasing difficulty. Addition of pinacolin to $NaNH_2$ in C_6H_6 followed by heating of the mixture until evolution of NH_3 ceases and gradual addition of $Pr^{\alpha}I$ gives ββ-*dimethylheptan-γ-one*, b.p. 168—172°, converted by further treatment with $NaNH_2$ and $Pr^{\alpha}I$ into ββ-*dimethyl-δ-propylheptan-γ-one*, b.p. 211—213°, and by $NaNH_2$ and MeI into ββδ-*trimethylheptan-γ-one*, b.p. 178—181°. *iso*Butyrone, $Pr^{\alpha}I$, and $NaNH_2$ in C_6H_6 give, according to conditions, βδδ-*trimethylheptan-γ-one*, b.p. 178—181°, or δδζζ-*tetramethylnonan-ε-one*, b.p. 229—232°. $COPr^{\beta}Bu^{\gamma}$ is converted by $Pr^{\alpha}I$ into ββδδ-*tetramethylheptan-γ-one*, b.p. 193—196°, but scarcely reacts with $Pr^{\alpha}I$. ββδδ-*Tetramethylhexan-γ-one*, b.p. 170—174°, is obtained from *iso*propylpinacolin or by two-fold methylation of $COPr^{\beta}Bu^{\beta}$. Repeated methylation of $COEtBu^{\beta}$ gives ββδδε-*pentamethylhexan-γ-one*, b.p. 195—197°. $COEt_2$ yields γε-*dimethylheptan-δ-one*, b.p. 170—173°, further ethylated to γε-*dimethyl-γ-ethylheptan-δ-one*, b.p. 204—207°. H. W.

Determination of acetylmethylcarbinol. A. F. Langlykke and W. H. Peterson (Ind. Eng. Chem. [Anal.], 1937, **9**, 163—166).—CHAcMe·OH is fairly volatile from aq. solution, *k* (Virtanen and Pulkki, A., 1929, 140) being 1·3, reacts quantitatively with alkaline I, reduces $CuSO_4$ (Stiles *et al.*, J. Bact., 1926, **12**, 427), requiring 2·95, and $K_3Fe(CN)_6$ (Hagedorn and Jensen, A., 1923, ii, 265), requiring 2·67 equivs. of H per mol., and is oxidised quantitatively by $K_2Cr_2O_7$ to AcOH. It is best determined in fermented products by direct distillation, and analysis of the third quarter of the distillate with alkaline I. A. Li.

Physalienone. P. Karrer and W. Gugelmann (Helv. Chim. Acta, 1937, **20**, 405—406).—Oxidation of physalien (zeaxanthin dipalmitate) with CrO_3 (≡4O) in C_6H_6–AcOH gives physalienone $[:(CH\cdot CH:CMe\cdot CH:)_2CH\cdot CO\cdot CMe_2\cdot CH_2\cdot CH(O\cdot C_{15}H_{31})\cdot CH_2Ac]_2$, m.p. 144—145°, which closes resembles β-carotenone in spectroscopic behaviour. It could not be hydrolysed satisfactorily with NaOEt. H. W.

Formation of carbohydrates by self-oxidation of hydrocarbons. N. A. Orlov and A. T. Shaligin (Compt. rend. Acad. Sci. U.R.S.S., 1937, **14**, 341—343).—When O_2 is passed through $CPh_2{:}CH_2$ (I) or $CPhMe{:}CH_2$ (II) at 50° CH_2O and $(CH_2O)_3$ can be detected in the H_2O through which the issuing gases are passed. Air saturated with (I) or (II) passed over Pt–Ni–Cr at 110° also gives CH_2O. The aq. extract of the product obtained by heating (I), diluted with sand and chalk, at 100—125° for 17 days gives positive tests for carbohydrates, and when (II) (64 g.) is similarly heated at 100—120° (50 days) the aq. extract contains 0·0231 g. of pentoses. J. W. B.

Determination of methoxyl in highly methylated carbohydrates. F. Neumann (Ber., 1937, **70**, [*B*], 734—736).—The substance (3—5 mg.) is weighed in a glass container into a slightly modified Pregl micro-methoxy-apparatus in which CO_2 is led to the bottom of the flask. The temp. is raised gradually to ≯80° during 30 min. and maintained at this point until the sample is completely dissolved. It is then heated gradually during 30 min. to boiling; after a further 15 min. it is certain that MeI is completely driven into the receiver. The results agree closely with those required by theory. The lower results obtained when heating is rapid are attributed to the resinification of the methylated carbohydrate and consequent shielding of part of the OMe from the acid. H. W.

Formation of *l*-threose. K. Iwadare, S. Fukunaga, and B. Kubota (Bull. Chem. Soc. Japan, 1937, **12**, 116—120).—*l*-Threose and its diacetamide have $[\alpha]_D^{20}$ +13·1° and +10·8° (equilibrium) (cf. Deulofeu, A., 1936, 826). F. R. G.

Carbon dioxide formation on boiling cellular matter with sulphite. O. Routala and T. Vauhkonen (Suomen Kem., 1937, **10**, B, 2).—On boiling Ca gluconate with SO_3'' a pentose, probably arabinose, is formed and CO_2 is evolved. E. A. H. R.

Comparative action of magnesia on sugars and glucosides. (Mlle.) M. Joly (J. Pharm. Chim., 1937, [viii], **25**, 457—465).—Glucose (I) is entirely or almost entirely (98%) destroyed by MgO in hot H_2O or aq. EtOH; three modifications of this method of removing (I) are detailed. Under similar conditions the following substances are destroyed to the extent stated: mannitol 27—60, fructose 80—98, sucrose 20—40, lactose 70—90, sorbitol 70—90, α- 5—15, and β-methylglucoside 0%. R. S. C.

Determination of glucose by dichromate. S. M. Strepkov (Biochem. Z., 1937, **290**, 91—94).—The $K_4Fe(CN)_6$ formed by interaction of the sugar with alkaline $K_3Fe(CN)_6$ is titrated with $K_2Cr_2O_7$ in acid solution using a solution of $NHPh_2$ in H_2SO_4 as indicator. The amount of $K_2Cr_2O_7$ used ∝ the amount of glucose present, 1 mg. of glucose being ≡ 0·65 c.c. of 0·05*N*-$K_2Cr_2O_7$. P. W. C.

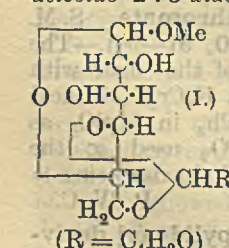
Formation of acetone [*iso*propylidene] derivatives of mercaptals. R. Sutra (Compt. rend., 1937, **204**, 783—785).—The rate of formation of *diisopropylidene*-d-*glucose* Et_2 *mercaptal* (I), $[\alpha]_{578}$

—48°, from $COMe_2$ and *d*-glucose Et_2 mercaptal with 0·1 and 0·01% of H_2SO_4 has been followed polarimetrically. The reaction is not of the first order. (I) is unstable and the $(SEt)_2$ could not be eliminated without affecting the $:CMe_2$ groups. In the similar formation of 2 : 3 : 5 : 6-di*iso*propylidene-*d*-mannose Et_2 mercaptal $[\alpha]_D$ passes through a min. val. J. W. B.

2 : 3 : 6-Trimethylglucose diethyl mercaptal. Its use in the preparation of 2 : 3 : 6-trimethylglucose. M. L. Wolfrom and L. W. Georges (J. Amer. Chem. Soc., 1937, 59, 601—603).—Methylcellulose and HCl (*d* 1·2) at 0—4° give 2 : 3 : 6-trimethylglucose, isolated as *Et$_2$ mercaptal*, m.p. 71—72°, $[\alpha]_D^{29}$ −15° in $CHCl_3$ (4 : 5-*dibenzoate*, m.p. 115—116°, $[\alpha]_D^{23}$ +61° in $CHCl_3$), readily hydrolysed to the pure S-free ether by $Cd(CO_3)_2$–$MgCl_2$. 2 : 3 : 4 : 6-Tetramethylglucose gives a *Et$_2$ mercaptal*, an oil (5-*benzoate*, m.p. 64—65°, $[\alpha]_D^{21}$ +33° in $CHCl_3$). R. S. C.

Transformation of hexoses into inositol. F. Micheel and H. Ruhkopf (Ber., 1937, 70, [*B*], 850—853; cf. A., 1935, 1225).—*d*-Galactose 6-*p*-toluenesulphonate is converted by $ZnCl_2$ and EtSH at 0° into d-*galactose Et$_2$ mercaptal* 6-p-*toluenesulphonate*, m.p. 115°, $[\alpha]_D^{20}$ +7·66° in C_5H_5N, transformed by Ac_2O and C_5H_5N at 0° into d-*galactose Et$_2$ mercaptal* 2 : 3 : 4 : 5-*tetra-acetate* 6-p-*toluenesulphonate*, m.p. 111°, $[\alpha]_D^{19}$ +4·0° in $CHCl_3$, which with $CaCO_3$–$HgCl_2$ in $COMe_2$ affords al-d-*galactose* 2 : 3 : 4 : 5-*tetra-acetate* 6-p-*toluenesulphonate* (I), m.p. 140—141°, $[\alpha]_D^{19}$ −17·60° in $CHCl_3$ {corresponding *Et$_2$ acetal*, m.p. 127° (decomp.), $[\alpha]_D^{18}$ −8·04° to +10·05° in EtOH–$CHCl_3$}. Condensation of (I) with Ac_2O–$ZnCl_2$ leads to *dl*-galactose hepta-acetate, m.p. 131°, thus confirming the mechanism of the transformation advanced previously (*loc. cit.*). H. W.

Carbohydrates and furfuraldehyde. III. Reactions with α-methylgalactoside, sorbitol, and mannitol. H. Bredereck and T. Papademetriu [with G. Rothe] (Ber., 1937, 70, [*B*], 797—802; cf. A., 1936, 192).—α-Methylgalactoside is converted by $CaCl_2$ and furfuraldehyde containing a little HNO_3 (*d* 1·2) at 160—165°/100—150 mm. into 4 : 6-*furylidene-α-methylgalactoside* (I), m.p. 160—161°, $[\alpha]_D^{20}$ +157·6° in H_2O. Its constitution follows from the following transitions. (I) is converted by Ac_2O–C_5H_5N at room temp. into 4 : 6-*furylidene-α-methylglucoside* 2 : 3-*diacetate*, m.p. 125—126°, transformed by successive treatments with HCl–EtOH and CPh_3Cl–C_5H_5N into 6-*triphenylmethyl-α-methylgalactoside* 2 : 3-*diacetate*, m.p. 85—87°, $[\alpha]_D^{20}$ +176·1° in $CHCl_3$, which gives the known 6-triphenylmethyl-α-methylgalactoside 2 : 3 : 4-triacetate, m.p. 179—181°. Alternatively, (I) is transformed by Ag_2O and MeI in $COMe_2$ into 4 : 6-*furylidene*-2 : 3-*dimethyl-α-methylgalactoside*, m.p. 138—140°, $[\alpha]_D^{20}$ +127·9° in $CHCl_3$, transformed by HCl–EtOH followed by CPh_3Cl–C_5H_5N into non-cryst. 2 : 3-*dimethyl*-6-*triphenylmethyl-α-methylgalactoside*.



(I.)

Sorbitol affords *tri*- (II), m.p. 186—187°, $[\alpha]_D^{21}$ +19·7° in $CHCl_3$, and *mono*- (III), m.p. 192—193°, *-furylidene-α-sorbitol*. Hydrolysis of (II) with AcOH in boiling EtOH give *difurylidene-α-sorbitol* (IV), m.p. 202—203°. Since (III) gives a $(CPh_3)_2$ derivative, m.p. 222—224°, it is assumed in analogy with monobenzylidenesorbitol to be the 2 : 4 derivative. (IV), which gives a CPh_3 derivative, is possibly the 2 : 4–5 : 6 compound and (II) is the 1 : 3–2 : 4–5 : 6 derivative. Mannitol gives *trifurylidenemannitol*, m.p. 176°, $[\alpha]_D^{18}$ −32·3° in $CHCl_3$, which could not be hydrolysed to the di-derivative, and *furylidenemannitol*, m.p. 126°, $[\alpha]_D^{21}$ +19·0° in H_2O; the constitutions are not elucidated. H. W.

Ketone sugar series. VI. Effect of zinc chloride on ketose acetates. F. B. Cramer and E. Pacsu (J. Amer. Chem. Soc., 1937, 59, 711—715; cf. A., 1935, 1484).—$ZnCl_2$ in Ac_2O equilibrates α- and β-acetates in the ketose as in the aldose series. [α] below are $[\alpha]_D^{20}$ in $CHCl_3$. Fructose α-, [α] +42·3°, and β-penta-acetate, [α] −122°, are equilibrated to a mixture, [α] −117°, from which both forms can be isolated. The second octa-acetate of turanose, [α] +106·5° in Ac_2O, gives an equilibrium mixture, [α] +98°, from which a syrup, [α] +63° in Ac_2O, is isolated; equilibration reconverts this into the mixture, [α] +98°; the existence of a new octa-acetate is inferred. The fourth turanose octa-acetate, [α] +103·2° in Ac_2O, gives a mixture, [α] +40°, from which much of the first octa-acetate, [α] +19·6°, is obtained. [α] of β-acetobromofructose (I) in C_5H_5N changes rapidly to −5·53° and then slowly to −45°; with C_5H_5N in EtOH a gel is transiently formed and the solution slowly acquires reducing properties. (I) and Ag_2O in MeOH give α- with much β-methylfructoside tetra-acetate. The relations of the acetates are discussed. R. S. C.

Reduction of α-*d*-glucoheptulose in presence of Raney's nickel. (Mme.) Y. Khouvine (Compt. rend., 1937, 204, 983—984; cf. A., 1934, 513).—α-*d*-Glucoheptulose (I) is incompletely reduced (Na–Hg) in a slightly acid medium, but in an alkaline medium α-glucoheptitol (II) and α-glucoheptulitol are formed rapidly. *d*-Sorbose with Raney Ni–H_2 in neutral or slightly alkaline solution affords *d*-sorbitol and *d*-iditol; the former reaction is slow. (I) with Raney Ni–H_2 in neutral or alkaline solution affords (II) and β-glucoheptitol completely. J. L. D.

Attempts to synthesise sucrose. F. Klages and R. Niemann (Annalen, 1937, 529, 185—204).—All the theoretically possible, sterically indisputable methods of synthesising 1-α-glucosido-2-β-fructofuranose fail; some methods lead to β-glucosido-α-fructofuranose, and this is negative evidence that sucrose has the former structure. Acetoglucosidyl bromide (I), fructose tetrabenzoate (II), and $Hg(OAc)_2$ do not react, (II) being inert. α-Glucose tetra-acetate, (II), and P_2O_5 even in complete absence of H_2O give ββ-trehalose octa-acetate with 12% of α-linkings, proving inversion of the tetra-acetate. α- or β-Glucose tetra-acetate (III) with EtBr–Ag_2CO_3 gives 75% of β- and 25% of α-ethylglucoside; fructose tetra-acetate gives mainly the α-form. (III) is converted into a 1 : 1 mixture of α- and

β-forms in C_6H_6. (II), (III), and Ag_2CO_3 give 1·3% of a disaccharide octa-acetate, m.p. 178°, $[\alpha]_D$ +56° in $CHCl_3$, formed entirely from (III), (II) being inert. (I) and $CH_2Ph{\cdot}OH$ in C_6H_6 give only the β-glucoside; acetofructosidyl halides give dextrorotatory benzyl-fructosides. Benzoylfructosidyl bromide, (III), and $Hg(OAc)_2$ do not react at 120°; at 150° decomp. begins, and no disaccharide is formed. R. S. C.

Synthesis of flavin glucosides. R. Kuhn and R. Ströbele (Ber., 1937, 70, [*B*], 747—752).—*d*-Arabinosido-2-nitro-4 : 5-dimethylanilide triacetate in MeOAc containing NEt_3 is reduced (PtO_2) and the filtered solution is treated with alloxan monohydrate and H_3BO_3 in AcOH, thereby giving 6 : 7-*dimethyl*-9-d-*arabinosidoflavin triacetate* (yield 60—65%), m.p. 240° (decomp.), $[\alpha]_D^{18}$ −453°±10° in MeOAc, $[\alpha]_D^{20}$ −510°±15° in 0·1*N*-NaOH, hydrolysed by NH_3 in abs. MeOH to 6 : 7-*dimethyl*-9-d-*arabinosidoflavin* (+1H_2O), $[\alpha]_D^{20}$ −418°±5° in C_5H_5N. 6 : 7-*Dimethyl*-9-l-*arabinosidoflavin triacetate*, m.p. 239°, $[\alpha]_D^{18}$ +440° ±10° in MeOAc, $[\alpha]_D^{22}$ +519°±15° in 0·1*N*-NaOH, $[\alpha]_D^{22}$ +352°±15° in 0·1*N*-NaOH + $Na_2B_4O_7$, readily hydrolysed by 0·1*N*-HCl, and 6 : 7-*dimethyl*-9-l-*arabinosidoflavin* are similarly obtained. 6 : 7-*Dimethyl*-9-dl-*arabinosidoflavin triacetate* has m.p. 260°. 6 : 7-*Dimethyl*-9-d-*ribosidoflavin* (I), $[\alpha]_D^{20}$ +470°±15° in C_5H_5N, gives a yellow solution with intense green fluorescence in H_2O. It is readily hydrolysed by cold dil. AcOH to *d*-ribose and 6 : 7-dimethylalloxazine and is very sensitive to 0·1*N*-NaOH. These flavin-9-glucosides are much more readily affected by light than is lactoflavin (II). (I) is reduced by $Na_2S_2O_4$ in neutral solution to a colourless leuco-compound which regenerates the pigment when shaken with air. Biologically it cannot replace (II); it does not promote growth in rats on a vitamin-B_2-free diet and does not give a catalytically active chromoprotein with the colloidal carrier of the yellow enzyme. H. W.

***o*-Nitroanilinoglucosides.** R. Kuhn and R. Ströbele (Ber., 1937, 70, [*B*], 773—787).—The condensation products of o-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and 2-nitro-4 : 5-dimethylaniline with pentoses and hexoses are glucosides since they afford tri- and tetra-acetates, respectively, and not tetra- and penta-acetates, which would result from Schiff's bases. Since the pentosides afford CPh_3 derivatives they are furoid in structure and the pyranoid constitution is assumed but not proven for the hexosides. The condensation is greatly impeded by the presence of o-NO_2, but the difficulty is overcome by use of NH_4Cl (2—3%) as catalyst in boiling abs. EtOH. Free HCl and NH_2Ph,HCl cause decomp.; NH_2Me,HCl is about as active as NH_4Cl, but $NHMe_2$,HCl and NMe_3,HCl are less efficient. In all cases an equilibrium is attained and the yields are improved by using an excess of base or by chromatographic removal of the glucoside from the equilibrium mixture and treatment of the filtrate with more NH_4Cl; yields then reach 80%. The m.p. of the glucosides are repeatable only under strictly defined conditions of crystallisation and desiccation, but they are readily characterised by their acetates. They are partly hydrolysed by hot H_2O, very readily by acids. Reduction to the compounds $NH_2{\cdot}C_6H_2Me_2{\cdot}NH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_n{\cdot}CH_2{\cdot}OH$ is effected in presence of Raney Ni, of Ni–Co–Cr, or of pure Ni, but for laboratory purposes the use of Pd–$CaCO_3$ or Pd–$BaSO_4$ is recommended since, although they are not the most efficient, they are most readily obtained with uniform properties. The most active catalyst is $Pd(OH)_2$, $Zn(OH)_2$, and $Cu(OH)_2$ on $CaCO_3$. The yields are greatly improved by use, during hydrogenation, of NaH_2BO_3, which forms complexes with the glucosides. The following compounds are described: 2-*nitro*-4 : 5-*dimethylanilino*-d-*arabinose*, softens at 111° (slight decomp.), $[\alpha]_D^{20}$ −20°±3° in C_5H_5N, and its *triacetate*, m.p. 212°, $[\alpha]_D^{20}$ −137°±5° in MeOAc; 2-*nitro*-4 : 5-*dimethylanilino*-l-*arabinose* (I), first *modification*, m.p. 111°, $[\alpha]_D^{18}$ +26°±3° in C_5H_5N, and its *triacetate* (II), m.p. 212°, $[\alpha]_D^{20}$ +139° ±5° in MeOAc, second *variety*, m.p. 186° (decomp.), $[\alpha]_D^{20}$ +76·0°±1° in C_5H_5N, converted by Ac_2O–C_5H_5N into (II); 2-*nitro*-4 : 5-*dimethylanilino*-dl-*arabinose triacetate*, m.p. 213—214°; 2-*nitro*-4 : 5-*dimethylanilino*-d-*ribose* (III), m.p. 164° when cautiously heated, $[\alpha]_D^{20}$ +90°±3° in C_5H_5N, and its *triacetate*, m.p. 163°, $[\alpha]_D^{20}$ +160°±5° in MeOAc; *o-nitroanilinoglucose*, m.p. 70—75°, and its *tetra-acetate*, m.p. 184°, $[\alpha]_D^{20}$ −75·2°±1° in MeOAc; *o-nitroanilino*-l-*arabinose*, m.p. indef., and its *tri-acetate*, m.p. 151°, $[\alpha]_D^{20}$ +133·8°±1° in MeOAc; *o-nitroanilino*-d-*xylose triacetate*, m.p. 149°, $[\alpha]_D^{21}$ −109·5°±2° in MeOAc; 2-*nitro*-4 : 5-*dimethylanilino*-d-*glucose*, m.p. 214° (decomp.), $[\alpha]_D^{21}$ +11·7° in C_5H_5N, and its *tetra-acetate*, indef. m.p. $[\alpha]_D^{22}$ −65·1°±0·5° in MeOAc; 2-*nitro*-4 : 5-*dimethylanilino*-d-*mannose*, indef. m.p., $[\alpha]_D^{20}$ −41·1°±1° in MeOAc, its *tetra-acetate*, m.p. 218°, $[\alpha]_D^{22}$ −93·8°±0·5° in MeOAc, and CPh_3 derivative, m.p. 130° (decomp.). The reduction of (I) and its subsequent condensation with alloxan and H_3BO_3 in AcOH to 6 : 7-*dimethyl*-9-l-*araboflavin*, m.p. 310° (decomp.), $[\alpha]_D^{25}$ −72·5°±2° in 0·1*N*-NaOH, are described. (III) similarly affords lactoflavin (yield 60%) identical with the natural product. H. W.

Water-soluble polysaccharide from barley leaves. W. N. Haworth, E. L. Hirst, and R. R. Lyne (Biochem. J., 1937, 31, 786—788).—The polysaccharide extracted from barley leaves by cold H_2O gives a methylated *derivative* (OMe 43·0%), $[\alpha]_D^{20}$ −50° in $CHCl_3$, which on hydrolysis yields 1 : 3 : 4-trimethylfructofuranose. It is constituted therefore of fructofuranose units linked together by bonds each of which engages the reducing group of one unit (C_2) and the $C_{(6)}$ position of the contiguous unit, and is closely related to if not identical with the lævan derived from the synthetic action of *B. mesentericus* (A., 1934, 760, 1338). Ketose determinations gave vals. equiv. to 93% of the total sugar and a small amount of a non-ketose sugar is probably present. The polysaccharide gives acetates of widely different rotations by varying the proportions of H_2O in the acetylation mixture; *e.g.*, 0·25 g. in 0·5 ml. of H_2O with C_5H_5N (5 ml.) and Ac_2O (5 ml.) gave an acetate with $[\alpha]_D^{20}$ +11° in $CHCl_3$, whereas with 1 ml. of H_2O the product had $[\alpha]_D^{20}$ −27° in $CHCl_3$. P. W. C.

Polysaccharides. XXIII. Determination of the chain length of glycogen. W. N. Haworth, E. L. Hirst, and F. A. Isherwood (J.C.S., 1937, 577—581).—Methylation (Me_2SO_4–NaOH in $COMe_2$) of rabbit-liver glycogen, followed by hydrolysis (MeOH–HCl) and determination of the yields of tri- and tetra-methylmethylglucoside, indicates a chain length of 18 α-glucopyranose units linked in the 1 : 4 position. J. D. R.

" Terminal group " method of W. N. Haworth and H. Machemer with polysaccharides. K. Hess and F. Neumann (Ber., 1937, **70**, [*B*], 710—721).—The cellulose acetate, sol. in $COMe_2$, used as initial material by Haworth and Machemer (A., 1932, 1022) is unsuitable for the decision of the presence of ring or chain since during its prep. (treatment of cotton with Ac_2O–SO_2Cl_2 and subsequent partial removal of Ac by H_2O–H_2SO_4) some disintegration of the cellulose (I) is unavoidable and the products are not completely removed by the subsequent procedure. It is uncertain to what degree the terminal group content of (I) is affected by these impurities. A quant. separation of tetramethylmethylglucoside from the other methylated sugars is not possible by Haworth's method. Within limits there is an enrichment of the head fractions in Me_5 ether but considerable amounts remain in the intermediate fractions. These cannot be evaluated by OMe or *n* since less highly methylated materials are unavoidably present in addition to Me_4 ethers. H. W.

Detection of the smallest quantities of terminal groups in polysaccharides. F. Neumann and K. Hess (Ber., 1937, **70**, [*B*], 721—727).—Attempts to separate permethylated (I) from incompletely methylated sugars by treatment of the latter with *p*-$C_6H_4Me{\cdot}SO_2Cl$, BzCl, etc. followed by fractional distillation are unsatisfactory since the two classes of compound are not sufficiently dissimilar in properties and (I) is very firmly retained by the esters. The carbohydrate therefore is once methylated (apparatus described), whereby it acquires 42% OMe equiv. to complete etherification of about 72% of all the free OH of cellulose, and the % terminal group found is then applied to 72% of the initial material. Further methylation is considered inadvisable in view of probable simultaneous degradation. The methylated product is converted by 42% HCl–H_2O into a mixture of methylated sugars transformed by 1% HCl–MeOH into the methylglucosides. The main portion of the less completely methylated sugars is removed by one or two fractional distillations. The glucosides are hydrolysed by 5% HCl–H_2O with the object of removing most of the 2 : 3 : 6-trimethylglucose by crystallisation. The mother-liquor residues are treated with 1% HCl–MeOH and then successively with $POCl_3$ and C_5H_5N and with $Ba(OH)_2$. The salt is washed with Et_2O or light petroleum whereby (I) are removed. They are treated with Na in C_6H_6 and then distilled in a vac. (~ 10^{-3} mm.; bath temp. 40—60°) over Na and weighed (two types of apparatus described). *Ba* 2 : 3 : 6-*trimethylmethylglucoside* 4-*phosphate* has been prepared. The separation of synthetic mixtures of 2 : 3 : 6-trimethyl- and 2 : 3 : 4 : 6-tetramethyl-methylglucoside is described. H. W.

Cellulose. LV. The terminal group question and constitution of cellulose. K. Hess and F. Neumann (Ber., 1937, **70**, [*B*], 728—733).—Application of the author's method of determining " terminal groups " to cellulose (I) of varied origin gives widely differing amounts of pentamethylglucose (II) if air is not excluded during the process. In the absence of air the formation of (II) could not be detected. Therefore either the mol. chain of (I) is so long that the formation of (II) is undetected (which necessitates the presence of many thousands of C_6 groups) or the mol. of (I) is cyclic and contains a completely unknown no. of units. The latter assumption is the more probable. H. W

Triphenylmethyl ether of cellulose. P. P. Schorigin, A. E. Veitzman, and N. N. Makarova-Zemlianskaja (J. Gen. Chem. Russ., 1937, 7, 430—439).—Cellulose 6-CPh_3 ether does not combine with Na or CS_2; it gives a Me_1 ether with Me_2SO_4 in aq. NaOH, or with MeI and Ag_2O, whilst further methylation leads to replacement of CPh_3 by Me. An attempted prep. of cellulose 6-triphenylmethyl 2 : 3-dimethyl ether from the 2 : 3-Me_2 ether was unsuccessful. Sakaruda's results (A., 1935, 201) were confirmed. R. T.

Werner complexes. Substitutions in optically active chlorinated complexes.—See A., I, 322.

Preparation of diacetylethylenediamine. L. H. Amundsen (J. Chem. Educ., 1937, **14**, 141—142).—Details of the prep. from 60—70% $(CH_2{\cdot}NH_2)_2$ and glacial AcOH are given. L. S. T.

Aliphatic polyamines. IV. J. van Alphen (Rec. trav. chim., 1937, **56**, 343—350; cf. A., 1936, 1274).—Interaction of $CH_2(CH_2Br)_2$ and $(CH_2{\cdot}NH_2)_2,H_2O$ (cf. A., 1936, 1493) affords *NN'*-di-β'-aminoethylpropylene-αγ-diamine, *NN'*-di-γ'-(β''-aminoethyl)aminopropylethylenediamine (I), b.p. 252°/14 mm. (*hydrochloride*, m.p. 275°; *H oxalate*, m.p. 235°; *picrate*, m.p. 220°, and *phenylthiocarbamide*, m.p. 135—140°), a fraction, b.p. 316°/14 mm., which contains a little *di*-β'-(γ'-β'''-*aminoethylaminopropyl*)*aminoethylpropylene*-αγ-*diamine* (isolated as the *hydrochloride*, m.p. >300°, of its *dibenzyl* derivative), but is mainly 1 : 4 : 8 : 11-*tetra-aza*cyclo*tetradecane*, $[CH_2]_2<^{NH{\cdot}[CH_2]_3{\cdot}NH}_{NH{\cdot}[CH_2]_3{\cdot}NH}>[CH_2]_2$ (II), b.p. 316°/14 mm. [*picrate*, decomp. 210°; *H oxalate*, decomp. 221°; *phenylthiocarbamide*, decomp. 138—140°; *hydrochloride* ($+1H_2O$); and *nitrate*, m.p. 205° (decomp.)], and fractions, b.p. 244°/16 mm. and 275°/16 mm., which probably resemble (II) in structure. With CS_2 in EtOH (I) gives an amorphous product converted by heat into 1 : 3-*di*-(γ-1'-*thiotetrahydroglyoxalinyl*)-*propylthiotetrahydroglyoxaline*, m.p. 166—167°, and with PhCHO in EtOH containing dissolving Na (I) affords the *CH₂Ph* derivative [$+2H_2O$, m.p. 54°; *hydrochloride*, m.p. >300° (decomp.); *nitrate*, m.p. 211°; *picrate*, m.p. 211°, and $(NO)_6$-derivative, m.p. 86°]. J. L. D.

Halogeno-salts of rhodium.—See A., I, 322.

Separation of choline and ethanolamine. E. Chargaff (J. Biol. Chem., 1937, **118**, 417—419).—Mixed hydrochlorides of choline (I) and ethanolamine

(II) in H_2O are treated with $NaHCO_3$ and $CHCl_3$, and $CH_2Ph{\cdot}O{\cdot}COCl$ is added, followed after 1 hr. by HCl. (I) can then be determined in the H_2O layer (as enneaiodide, aurichloride, platinichloride, or perchlorate), and from the $CHCl_3$ *carbobenzyloxyethanolamide*, m.p. 66·5°, be isolated, and converted into (II) (aurichloride) by Pd–H_2 reduction.

E. W. W.

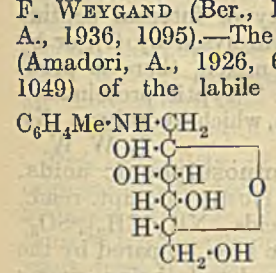
Methylcholines. Oxidation with permanganate. E. Kahane (Bull. Soc. chim., 1937, [v], **4**, 717—727).—Oxidation of choline perchlorate with 0·1*N*-$KMnO_4$ (1·45 atoms of O) in presence of 1—2 c.c. of 10% H_2SO_4 at room temp. affords betaine (I), and α-methylcholine chloride (II) similarly takes up 1·68 atoms of O to give $^+NMe_3{\cdot}CHMe{\cdot}CO_2^-$. Under these conditions the chlorides of β-methylcholine (III), its Ac derivative, and acetylcholine are unattacked, although in more strongly acid solution (III) absorbs 5 O to give (I). By use of this method it is found that the products obtained by the action of NMe_3 on chloropropyl alcohols obtained in various ways are all essentially the same and contain only 5—6% of (II).

J. W. B.

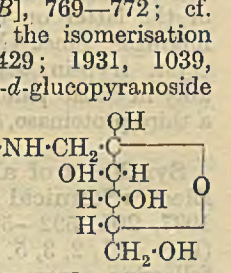
Isolation of glucosamine. E. Chargaff and M. Bovarnick (J. Biol. Chem., 1937, **118**, 421—426).—Aq. glucosamine hydrochloride (I) with $NaHCO_3$ and $CH_2Ph{\cdot}O{\cdot}COCl$ (II) gives *carbobenzyloxyglucosamide*, m.p. 214° (decomp.) (corr.), $[\alpha]_D^{24}$ +62·8° → +75·4° in C_5H_5N, which with Pd–H_2 yields 93% of the original (I). (II) does not give insol. derivatives with *l*-arabinose, *d*-ribose, *d*-xylose, *d*-glucose, *d*-mannose, *d*-galactose, *d*-fructose, or glucuronogalactose, and may therefore be used to separate (I) from these sugars; a method of separation from mixed sugars, and the identification of the latter in the residue, are described. (II) may be used to separate (I) from glycine, as the carbobenzyloxy-derivative of the latter is not pptd. until HCl is added.

E. W. W.

The Amadori transformation. R. Kuhn and F. Weygand (Ber., 1937, **20**, [*B*], 769—772; cf. A., 1936, 1095).—The product of the isomerisation (Amadori, A., 1926, 60; 1929, 429; 1931, 1039, 1049) of the labile *p*-toluidino-*d*-glucopyranoside



(I.) β-form



(I.) α-form

is identified as N-p-*tolyl*-d-iso*glucosamine* (I). It shows marked mutarotation in C_5H_5N and when oxidised with CrO_3 gives 0·6 mol. of AcOH. It is a very powerful reducing agent resembling ascorbic acid in its conversion of o-$C_6H_4(NO_2)_2$ in alcoholic alkaline solution into o-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}OH$. It is remarkably stable to HCl, which does not induce simple hydrolysis. It yields an *oxime*, m.p. 135—136°, $[\alpha]_D^{19\cdot5}$ −21° in C_5H_5N. It is reduced to N-p-*tolyl*-d-*mannamine*, m.p. 194—195°, $[\alpha]_D^{21}$ +28·8° in C_5H_5N, also obtained by condensing p-$C_6H_4Me{\cdot}NH_2$ with mannose in boiling EtOH containing NH_4Cl to p-*toluidino*-d-*mannoside*, m.p. 184°, $[\alpha]_D^{20}$ −181° in C_5H_5N, and hydrogenation of the latter. The Amadori isomerisation affords a new transition from the *d*-glucose to the *d*-fructose series.

H. W.

Chemical comparison between chitin and cellulose. K. H. Meyer and H. Wehrli (Helv. Chim. Acta, 1937, **20**, 353—362).—Chitin (I) undergoes slight deacetylation during its prep. by treatment of the shells of crustaceæ with dil. NaOH followed by dil. HCl and finally by EtOH. It has Cu no. 1·5. Determinations of the mol. wt. of (I) by osmotic measurements is impossible since it is decomposed by long contact with available solvents but measurements of viscosity indicate a val. comparable with that of cellulose (II) derived from wood by chemical methods. The heat of activation of the acidic hydrolysis of (I) is practically identical with that of (II) and in good agreement with the presence of the same type of β-linkings in (I) and (II). (I) is sol. only in mineral acids, in which it becomes degraded, and is unaffected by the mineral solvents of (II). A process comparable with mercerisation is not observed with (I). Esterification of (I) is much more difficult than that of (II). Prolonged treatment of (I) with conc. NaOH causes almost complete elimination of Ac, giving a polyglucosamine (III) which according to Cu no. and viscosity contains about 25 sugar residues. The corresponding hydrochloride, although cryst., is derived from a complex base which is thus analogous to the oligosaccharide obtained by degradation of cellulose acetate. Deamination of (III) under very mild conditions gives a substance of low mol. wt. which yields glucosephenylosazone with $NHPh{\cdot}NH_2$; transformation of NH_2 into OH is thus accompanied by hydrolysis of the glucosidic linking.

H. W.

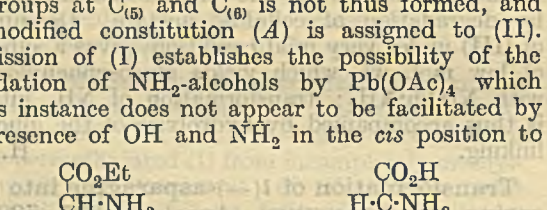
Transformation of *l*(−)-asparagine into *l*(−)-serine. F. Schneider (Annalen, 1937, **529**, 1—10).—Carbobenzyloxy-*l*-asparagine is converted by NaOCl at 60° into *carbobenzyloxy-l-glyoxalidonecarboxylic acid* (I), $\begin{matrix}CH_2{\cdot}CH(CO_2H)\\ NH{\cdot}CO\end{matrix}\!\!>\!N{\cdot}CO_2CH_2Ph$, m.p. 194°, hydrolysed by HCl to *l*(+)-diaminopropionic acid monohydrochloride (II), $[\alpha]_D^{20}$ +25·25° ±0·2° in *N*-HCl. (I) is transformed by H_2 in presence of Pd-sponge into *l*-(−)-glyoxalidone-2-carboxylic acid, m.p. 190—191° (decomp.), $[\alpha]_D^{19}$ −16·0°±0·2°. (II), $ClCO_2CH_2Ph$, and KOH afford l-αβ-*dicarbobenzyloxamidopropionic acid*, m.p. 99—100°, converted by PCl_5 in $CHCl_3$ into the corresponding *anhydride*, which is transformed by 5*N*-HCl–MeOH into *Me* l-α-*amino*-β-*carbobenzyloxamidopropionate hydrochloride*, m.p. 164°. This is converted by BzCl–MgO in H_2O–$CHCl_3$ into *Me* l-α-*benzamido*-β-*carbobenzyloxamidopropionate*, m.p. 102°, hydrogenated (Pd-sponge) to *Me* l-β-*amino*-α-*benzamidopropionate hydrochloride*, m.p. 179° (decomp.), which is transformed by the successive action of $Ba(NO_2)_2$–HCl and 16% HBr at 140° into *l*(−)-serine, $[\alpha]_D^{20}$ −7·20°± 0·25° in H_2O, +14·75°±0·30° in H_2O + *N*-HCl. *l*(−)-Asparagine, *l*(+)-αβ-diaminopropionic acid, and *l*(−)-serine are therefore configuratively related.

H. W.

Constitution of the copper salts of aspartic and glutamic acids. P. Pfeiffer and H. Werner

(Z. physiol. Chem., 1937, **246**, 212—218).—Aq. Cu aspartate (I), $(C_4H_5O_4N)_2Cu_2,9H_2O$ (1 mol.), with dil. NaOH (<2 mols.) affords $Cu(OH)_2$ and a blue-violet solution containing a substance (pptd. by EtOH) with Cu : Na : N = 1 : 2 : 2, also yielded by (I) + Na aspartate [corresponding Ba salt prepared from (I) + Ba aspartate]. Hence (I) is $[Cu(C_4H_5O_4N)_2]Cu$ whilst parallel reactions indicate Cu glutamate to be $[Cu(C_5H_7O_4N)_2]Cu$. Structural formulæ for the two complex salts are suggested. F. O. H.

New degradation of glucosamic acid. Configuration of glucosamic and chondrosamic acid. P. KARRER and J. MAYER (Helv. Chim. Acta, 1937, **20**, 407—417).—Et benzylideneglucosamate hydrochloride is transformed by NaOH and $ClCO_2Et$–Na_2CO_3 into the N-*carbethoxy*-derivative (I), m.p. 129°, which is oxidised by $Pb(OAc)_4$ in C_6H_6 to *Et carbethoxyaminohydroxyacetate*, $CO_2Et{\cdot}NH{\cdot}CH(OH){\cdot}CO_2Et$, m.p. 87° (transformed by *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ into the *p*-nitrophenylhydrazone and semicarbazone, respectively, of glyoxylic acid and oxidised by I to $H_2C_2O_4$). Benzylideneglucosamic acid does not therefore contain free OH at $C_{(3)}$ and $C_{(4)}$. Since its Et ester (II) is transformed by Ac_2O in C_5H_5N into a Ac_3 derivative, m.p. 115°, which after removal of :CHPh with 60% AcOH does not give CH_2O when oxidised by HIO_4 it follows that a compound with free OH groups at $C_{(5)}$ and $C_{(6)}$ is not thus formed, and the modified constitution (*A*) is assigned to (II). The fission of (I) establishes the possibility of the degradation of NH_2-alcohols by $Pb(OAc)_4$ which in this instance does not appear to be facilitated by the presence of OH and NH_2 in the *cis* position to



(*A*.) (*B*.)

one another. The behaviour of glucosamic dipeptide to dipeptidase indicates the *d*-glucose configuration with NH_2 and OH at $C_{(2)}$ and $C_{(3)}$ in the *trans* position in glucosamic acid. Confirmation is obtained from the rotation dispersion and Cotton effect of Cu glucosamate, which assign it to the *d*-NH_2-acid series. The analogous behaviour of Cu chondrosamate indicates the configuration (*B*) for chondrosamic acid (III). (III) or its ester could not be caused to react with PhCHO or *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ but treatment of (III) in NaOH with Ac_2O yields N-*acetylchondrosamolactone*, m.p. 165°, which does not afford a :CHPh compound but is transformed by 1% HCl–$COMe_2$ into N-*acetylisopropylidenechondrosamolactone*, m.p. 164°. H. W.

Proteolytic enzymes. XIII. Synthetic substrates for chymotrypsin. M. BERGMANN and J. S. FRUTON (J. Biol. Chem., 1937, **118**, 405—415).—Cryst. chymotrypsin (I) hydrolyses *carbobenzyloxyglycyl*-l-*tyrosylglycineamide* (II), m.p. 192°, obtained by hydrogenating N-*carbobenzyloxy*-O-*acetyl*-l-*tyrosylglycine Et ester* (III), m.p. 127° (from the *l*-tyrosyl chloride and $NH_2{\cdot}CH_2{\cdot}CO_2Et$); one peptide linking is broken, giving carbobenzyloxyglycyl-*l*-tyrosine, further hydrolysed by cryst. carboxypeptidase to tyrosine (cf. animal digestion of proteins). [For further hydrolyses by (I), see below.] Papain–HCN hydrolyses (II) to carbobenzyloxyglycine and *l*-tyrosylglycine. (II) is hydrogenated to *glycyl*-l-*tyrosylglycineamide hydrochloride* (IV), m.p. 89—90°. (III) is converted by NH_3–MeOH into *carbobenzyloxy*-l-*tyrosylglycineamide* (V), m.p. 116°, which with (I) gives N-*carbobenzyloxytyrosine* (an oil). With MeOH–NaOH, (III) gives *carbobenzyloxy*-l-*tyrosylglycine* (VI), m.p. 100°. Tyrosine Et ester with carbobenzyloxyglycyl chloride yields *carbobenzyloxyglycyl*-l-*tyrosine Et ester*, m.p. 118°, hydrolysed by NaOH to *carbobenzyloxyglycyl*-l-*tyrosine*, m.p. 107°. Carbobenzyloxy-*l*-tyrosine Et ester with N_2H_4,H_2O forms *carbobenzyloxy*-l-*tyrosylhydrazide*, m.p. 220°; this with $NaNO_2$–HCl forms the *azide*, which with glycylglycine Et ester yields *carbobenzyloxy*-l-*tyrosylglycylglycine Et ester*, m.p. 165°, converted by NH_3–MeOH into the *amide* (VII), m.p. 218°. Carbobenzyloxy-*l*-phenylalanyl chloride and glycine Et ester form *carbobenzyloxy*-l-*phenylalanylglycine Et ester*, m.p. 111°, which on hydrogenation and treatment with carbobenzyloxyglycyl chloride gives *carbobenzyloxyglycyl*-l-*phenylalanylglycineamide* (VIII), m.p. 178°. *Carbobenzyloxyglycyl*-l-*glutamylglycineamide* (IX), obtained from the ester, has m.p. 175°.

(IV) and (V) are readily hydrolysed by (I), (VII) and (VIII) much more slowly; (VI) and (IX), and benzoylglycyl-*l*-lysineamide (X), carbobenzyloxyglycyl-*l*-leucylglycineamide, benzoyl-*l*-leucyl-*l*-leucylglycine, and chloroacetyltyrosine are not attacked. From the above, (I) is shown to be a peptidase, *i.e.*, proteinases are endopeptidases (cf. A., 1936, 1152). That (I) distinguishes between phenylalanyl and leucyl, and similar differentiations, must depend not on combination of enzyme with side-chain, but on the effect of the latter on the sensitivity of internal peptide linkings. Since (X) is not hydrolysed by (I), or by cryst. trypsin, separately or mixed, there is probably in cattle pancreas and in "tryptic proteinase" a third proteinase, *heterotrypsin*, which hydrolyses (X). E. W. W.

Synthesis of aliphatic aminosulphonic acids. Electrochemical study. P. RUMPF (Compt. rend., 1937, **204**, 592—595).—The acids $^+NH_3{\cdot}[CH_2]_n{\cdot}SO_3^-$ (I) (n = 1, 2, 3, 5, and 10) have been prepared by the following general methods, no details being given: (*a*) $(CH_2)_m{>}NH$ and aq. H_2SO_3 afford $NH_2{\cdot}[CH_2]_m{\cdot}SO_3H$ when m = 2 or 3; (*b*) action of NH_3 on *γ-chloro*-n-*propane*-*α*-*sulphonyl chloride*, b.p. 124—127°/15 mm. (from $OH{\cdot}[CH_2]_3{\cdot}SO_3Na$); (*c*) by the action of conc. aq. Na_2SO_3 on halogenoalkylphthalimides and hydrolysis of the sulphonated amides so obtained; thus $NHBz{\cdot}[CH_2]_4{\cdot}CH_2Cl$ gives *ε-amino*-n-*pentane*-*α*-*sulphonic acid*, m.p. approx. 310°, and *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_3Br$ affords *γ-amino*-n-*propane*-*α*-*sulphonic acid*; (*d*) from β-, γ-, or δ-sulphoacids by conversion of CO_2H into NH_2 with N_2H–conc. H_2SO_4–$CHCl_3$ at 45°; thus χ-bromoundecoic acid is converted through the χ-SO_3H derivative into *χ-amino*-n-*decane*-*α*-*sulphonic acid*, m.p. approx.

340° (decomp.) (block). The vals. of $-\log K_{II}$ for (I), determined by electrometric titration of 0·1*N* solution with *N*-NaOH using a glass electrode, are approx. 1, 5·75 (±0·05), 9·30, 10·05, 10·95, and 11·35 (±0·2) when $n = 0, 1, 2, 3, 5$, and 10, respectively, and approx. 5·8 and 1·4 for $^{+}NH_3{\cdot}CHMe{\cdot}SO_3^{-}$ and $^{+}NH_2Ph{\cdot}CH_2{\cdot}SO_3^{-}$, respectively. J. W. B.

Synthesis of α-glutamylcysteinylglycine (*iso*-glutathione). V. DU VIGNEAUD, H. S. LORING, and G. L. MILLER (J. Biol. Chem., 1937, **118**, 391—395).—*S*-Benzylcysteinylglycine (A., 1935, 1486) and carbobenzyloxyglutamic anhydride in C_5H_5N give *N-carbobenzyloxy-α-glutamyl-S-benzylcysteinylglycine*, m.p. 191—192°, which is also obtained from γ-Et *N*-carbobenzyloxyglutamate (A., 1933, 1039, 1281) by conversion into the acid chloride and combination with *S*-benzylcysteinylglycine Me ester, and which with Na in liquid NH_3 yields *α-glutamylcysteinylglycine* (*isoglutathione*), m.p. 152—153° (decomp.), $[\alpha]_D^{25}$ +2·5° in H_2O. E. W. W.

Selenium-substituted amino-acids. II. Optically active forms of selenocystine. A. FREDGA (Svensk Kem. Tidskr., 1937, **49**, 124—130; cf. A., 1936, 1096).—(+)-*Selenocystine* (I), m.p. about 215°/decomp.) after softening at 180°, $[M]_D^{25}$ +573° in 0·5*N*-HCl (*hydrochloride*), has been obtained from *d*-serine. (+)-*Selenocystine* has $[M]_D^{25}$ −571°. An active *racemate* of (I) and (−)-cystine and its *hydrochloride* are described. M. H. M. A.

Catalytic hydrogenation of amides of α-hydroxy-acids. H. ÔEDA (Bull. Chem. Soc. Japan, 1937, **12**, 121—127).—*dl*-$OH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$ (A., 1936, 1092) was hydrogenated (A., 1935, 189) to $OH{\cdot}CHMe{\cdot}CH_2{\cdot}OH$, *αδ-diamino-βγ-dimethylbutane* [*picrate*, decomp. >260°; Bz_2 derivative, m.p. 227—228° (corr.)] and its N-*Pr* derivative (*picrate*, m.p. about 238°; *platinichloride*, decomp. 265—270°). Similarly *l*-$OH{\cdot}CHBu^{\beta}{\cdot}CO{\cdot}NH_2$ gave *l*-$OH{\cdot}CHBu^{\beta}{\cdot}CH_2{\cdot}OH$, dl-*αδ-diamino-βγ-diisobutylbutane*, m.p. 62—64° [*hydrochloride*, decomp. >330°; *picrate*, decomp. 248°; Bz_2 derivative, m.p. 223—224° (corr.); *platinichloride*, decomp. >330°], and an unidentified base giving a hydrochloride, m.p. 220—230° (decomp.). F. R. G.

Precipitability of complex trithiocarbamide cuprochloride from its aqueous solution. E. STORFER (Monatsh., 1937, **70**, 236—250).—Aq. solutions of trithiocarbamide cuprochloride (I) give ppts. when treated with org. and inorg. compounds with dissociation const. $>10^{-3}$; certain exceptions are recorded. The upper and lower limits of concn. of uni-, bi-, ter-, and quadri-valent ions required for the pptn. of (I) from H_2O and the "breadth of zone" are recorded. The *compounds* $C_5H_{24}O_6N_{10}S_6Cu_2$, $C_5H_{24}O_6N_{10}ClS_6Cu_2$, $C_8H_{28}O_6N_{12}S_6Cu_2$, $C_9H_{16}O_2N_{12}S_3Cu_3Fe$, and $C_{10}H_{22}O_3N_{14}S_4Cu_4Fe$ are obtained by adding K_2SO_4, $CuSO_4$, $K_2C_2O_4$, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ respectively to aq. solutions of (I). H. W.

Crystalline compound of semicarbazide and semicarbazide hydrochloride. H. L. HALLER and F. B. LAFORGE (J. Amer. Chem. Soc., 1937, **59**, 760).—Semicarbazide hydrochloride (I) and C_5H_5N in aq. EtOH give a 1 : 1 additive *compound*, m.p. 132°, of (I) and semicarbazide. This may be formed when semicarbazides are prepared by C_5H_5N. With conc. HCl it gives (I). R. S. C.

Effect of certain substances on the formation of hydrocyanic acid by the oxidation of fructose or alloxan with ammoniacal copper salts. J. PARROD (Compt. rend., 1937, **204**, 871—873; cf. A., 1936, 968).—Fructose (I) and alloxan (II) with NH_3-$Cu(OH)_2$ in different solvents at 60° afford HCN. (II) gives the greater yield when dissolved in many mono- and di-carboxylic acids, and polyhydric alcohols. In H_2SO_3, (I) is the better source, and liberates more HCN the more prolonged is the reaction. When glycerol is the solvent, a rapid, initial reaction alone occurs. (II) liberates HCN throughout the duration of the reaction in either solvent. J. L. D.

Additive products of hydrocyanic acid with glucosylarylamines and glucosylpiperidines. E. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1937, **9**, 109—119).—Compounds of type $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_n{\cdot}CH(NHR){\cdot}CN$ are prepared from the reaction products of sugars and NH_2Ph. The product from *l*-arabinose gives, with anhyd. HCN in EtOH, *anilino-l-arabohexononitrile*, m.p. 150° (decomp.), $[\alpha]_D$ −157° (all rotations in MeOH). d-*Xylosylaniline*, m.p. 148°, $[\alpha]_D$ (extrapolated) −79·6°, falling to −24°, gives *anilino*-d-*xylohexononitrile*, m.p. 115—120°. The product from rhamnose and NH_2Ph gives *anilino*-l-*rhamnohexononitrile*, m.p. 143°, $[\alpha]_D$ −34·5°. l-*Fucosylaniline*, m.p. 150—151°, $[\alpha]_D$ (extrapolated) +102°, falling to +49°, yields *anilino*-l-*fucohexononitrile*, m.p. 173—174° (decomp.), $[\alpha]_D$ +156°. Mannosylaniline (simplified prep. from vegetable ivory) gives *anilino*-d-*mannoheptononitrile*, $[\alpha]_D$ +156°. The reaction products from piperidine with rhamnose and with mannose give respectively *piperidyl*-l-*rhamnohexono*-, m.p. 142—143°, $[\alpha]_D$ +27°, and-d-*mannoheptono-nitrile*, m.p. 125—127° (decomp.), $[\alpha]_D$ −10°. Anilinoglucoheptononitrile with Ac_2O–NaOAc gives an Ac_5 derivative, and anilinogalactoheptononitrile an Ac_5 derivative, m.p. 122°. Glucose and *m*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ yield d-*glucosyl*-m-*nitroaniline*, m.p. 172—186°, unchanged by HCN. E. W. W.

Esterification of hydrocobalticyanic acid with diazomethane. J. MEYER and O. RAMPOLDT (Z. anorg. Chem., 1937, **232**, 188—192).—In MeOH the reaction yields about 40% of β-$Me_3Co(CN)_6$. An incompletely methylated ester is also formed. E. S. H.

Carbon rings. XXXI. Relationships between m.p. and density in aliphatic and cyclic homologous series. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1937, **20**, 548—562).—Calculation of *d* for cyclic ketones between 120° and −80° shows that at the latter temp. a max. is not observed for the 10-membered ring. With increasing temp. the max. becomes gradually apparent and is very pronounced at 120°. There appears no reason to connect max. *d* with min. yield and it is doubtful whether general conclusions can be based on the val. of *d* at an arbitrarily chosen, fixed temp. The question of corresponding temp. is discussed and 20° > m.p. is chosen

in order to avoid undue departure from observed vals. Tables are given for *d* of *n*-paraffins, cyclic hydrocarbons, *n*-aldehydes and *n*-ketones, cyclic ketones, and diketones, lactones, polymethylene carbonates and dicarboxylic esters, and cyclic imines under this condition. The qual. course of the graphs is readily understood if it is assumed that the arrangement of the mols. in the liquid state is mainly conditioned by the no. of mols. in the unit of vol. and the probability of as close a packing of the mols. as possible; the resultant of these factors represents *d*. The close similarity of the graphs of aliphatic and cyclic compounds indicates that polymembered rings with an even no. of members are to be regarded as two halves of a 6-ring joined by two approx. parallel chains of CH_2 groups. Rings with an odd no. of members are represented as the two "halves" of a 5-ring formed in the same manner as shown above. Practical justification for the use of a corresponding temp. is afforded by the regularities between *d* and m.p. which then become obvious in a homologous series. H. W.

Aromatisation of certain homologues of *cyclo*pentane and of paraffins in presence of platinised charcoal. B. A. Kazanski and A. F. Plate (J. Gen. Chem. Russ., 1937, **7**, 328—334).—The following products are obtained by passing the hydrocarbons over Pt–C at 310—315°; δ-methyloctane and *o*-C_6H_4MeEt from *n*-butyl*cyclo*pentane; *p*-xylene from Bu^{β}_2; PhEt and *o*-xylene from *n*-octane; *m*-$C_6H_4MePr^{\beta}$ from di*iso*amyl. R. T.

Equilibrium and kinetics of diene synthesis.—See A., I, 313.

Autoxidation of cyclic ethylenic hydrocarbons. II. R. Dupont (Bull. Soc. chim. Belg., 1937, **46**, 21—26; cf. A., 1936, 712).—Autoxidation of 1 : 2-dimethyl-Δ^1-*cyclo*hexene at 70° for a week, followed by treatment with $Ba(OH)_2$ and distillation at 18 mm., yields chiefly 1 : 2-dimethyl-Δ^1-*cyclo*hexen-3-one (semicarbazone, m.p. 224°) and *trans*-1 : 2-dimethyl*cyclo*hexane-1 : 2-diol [oxidised to the ketone (semicarbazone, m.p. 223°)], with a little Ac·$[CH_2]_4$·Ac. A. Li.

Contact transformation of Δ^{γ}-butenyl*cyclo*hexane (δ-*cyclo*hexyl-Δ^{α}-butene). R. J. Levina and M. I. Tscherniak (J. Gen. Chem. Russ., 1937, **7**, 402—404).—δ-*cyclo*Hexyl-Δ^{α}-butene yields PhBu$^{\alpha}$ and *n*-butyl*cyclo*hexane when passed over Pt–C at 210° in CO_2. R. T.

Catalytic transformation of *cyclo*hexylacetylene. R. J. Levina and A. A. Potanova (J. Gen. Chem. Russ., 1937, **7**, 353—356).—*cyclo*Hexylacetylene yields PhEt and ethyl*cyclo*hexane when passed over Pt–C at 200°. R. T.

***cyclo*Heptane and hydrogenation–dehydrogenation catalysis.** M. B. Turova-Pollak (J. Gen. Chem. Russ., 1937, **7**, 369—371).—*cyclo*Heptane is gradually converted into methyl*cyclo*hexane, and this into PhMe, by repeated passage over Pt–C at 300—315°. R. T.

***cyclo*Hexyl*cyclo*pentane and its transformations during hydrogenation–dehydrogenation catalysis.** S. I. Chromov (J. Gen. Chem. Russ., 1937, **7**, 350—352).—The products obtained with H_2 at 300—310° (Pt–C catalyst) were $CHPhEt_2$ and α- and β-phenylpentane. R. T.

Isomerisation of di*cyclo*hexyl in presence of aluminium chloride. R. J. Levina, J. K. Juriev, and A. I. Loschkomoinikov (J. Gen. Chem. Russ., 1937, **7**, 341—349).—Di*cyclo*hexyl and $AlCl_3$ at 100° (50 hr.) yield chiefly trans-trans-*di*cyclo*hexyl*, b.p. 217—219°, from which 2 : 6-$C_{10}H_6Me_2$ is obtained by dehydrogenation (Pt catalyst at 310°). R. T.

Influence of *cyclo*hexene concentration in the alkylation of benzene by *cyclo*hexene. Dealkylation of *cyclo*hexylbenzenes. B. B. Corson and V. N. Ipatiev (J. Amer. Chem. Soc., 1937, **59**, 645—647).—The degree of alkylation of C_6H_6 by *cyclo*hexene (I) depends on the proportions used. $AlCl_3$ (60 g.), C_6H_6 (2·3), and (I) (3 mols.) at 3—18° give *cyclo*hexyl- (II) (58 g.), b.p. 238·6—238·8°/756 mm., m.p. 6·6—7°, 1 : 4-di*cyclo*hexyl- (III) (31 g.), b.p. 335—340°/756 mm., 1 : 3 : 5-*tri*- (IV) (158 g.), m.p. 68·5—69°, and 1 : 2 : 3 : 5-*tetra*-cyclo*hexyl-benzene* (V) (1 g.), m.p. 264—265°. 2 mols. of C_6H_6, 4 mols. of (I), and 60 g. of $AlCl_3$ in *cyclo*hexane (150 g.) give 80 g. of (V). With H_2SO_4 (II), (III), and (V) are obtained. Further reaction of (II) and (III) readily gives (V), but (IV) gives mostly oils. Dealkylation ($AlCl_3$ in C_6H_6) of (III) and (IV) gives (II), that of (V) gives (II) and (IV), a small amount of a *substance*, $C_{18}H_{20}$, m.p. 168—169°, being also obtained in all cases. The structure of (II) follows from its conversion by Br into Ph_2, that of (III) by dehydrogenation and hydrogenation (Ni; 220°/100 kg.) to di*cyclo*hexyl*cyclo*hexane (VI), forms, m.p. 159·5—161° and 54—56°, that of (IV) by conversion by Br into 1 : 3 : 5-$C_6H_3Ph_3$ and by hydrogenation (Ni; 240°/120 kg.) to 1 : 3 : 5-*tri*cyclo*hexyl*cyclo*hexane* (VII), m.p. 158—159°, and that of (V) by its dealkylation and by hydrogenation to give (VI) and (VII). R. S. C.

Formation of benzene in the radiochemical polymerisation of acetylene. W. Mund and C. Rosenblum (J. Physical Chem., 1937, **41**, 469—475).—C_2H_2 under the influence of α- and β-rays from Rn simultaneously polymerises into C_6H_6 and cuprene. C. R. H.

Benzenesulphonates of copper.—See A., I, 307.

Electrolytic hydrogenation of bromobenzene. M. Busch and W. Weber (Ber., 1937, **70**, [*B*], 744—746).—Electrolysis of alkaline-alcoholic solutions of PhBr at a Pd, Cu, Pb, or Hg cathode causes quant. removal of halogen at a rate which ∝ the overvoltage of the cathode. C_6H_6 unmixed with Ph_2 is produced. H. W.

Catalytic dehydrogenation of ethylbenzene to styrene. J. S. Salkind and G. L. Bulavski (Plast. Massui, 1935, No. 3, 9—12).—Passage of PhEt in N_2 over ZnO–Al_2O_3 (1 : 9) at 660—670°/10—13 mm. at the rate of 1 g. per min. yields 83% of styrene. Ch. Abs. (*r*)

αα′μμ′-Tetraphenyldodecahexaene. G. Wittig and R. Wietbrock (Annalen, 1937, **529**, 162—166).—$\Delta^{\beta\delta}$-Hexadiene-αζ-dicarboxylic acid, PbO, and CPh_2:CH·CHO in Ac_2O at 150° (CO_2) give orange-red αα′μμ′-*tetraphenyldodecahexaene*, m.p. 213—214·5°

[*octabromide*, m.p. 205—206° (decomp.)], which is reduced (PtO_2) to αααμ-*tetraphenyldodecane*, m.p. 74—75°, and is not readily oxidised. The hexaene is decolorised only after 9 hr. in boiling xylene; αααω-tetraphenyl-decapentaene and -octatetraene require boiling for 16 and 25 hr., respectively. Polyenes of this series absorb n — 2 mols. of Br, n being the no. of CH:CH. R. S. C.

Dipole measurements on isomeric plato-complexes. III.—See A., I, 322.

Synthesis of 8 : 8′-dinitro-1 : 1′-dinaphthyl and related compounds. H. H. Hodgson and J. H. Crook (J.C.S., 1937, 571—573).—8 : 1-NO_2·$C_{10}H_5$·NH_2 (I) in AcOH diazotised (conc. H_2SO_4) and treated with KI affords 1-*iodo*-8-*nitronaphthalene* (II), m.p. 80°, nitrated to 1-*iodo*-4 : 8-*dinitronaphthalene* (III), m.p. 146°, also produced by the Sandmeyer reaction on 4 : 8 : 1-$(NO_2)_2C_{10}H_5$·NH_2 (IV). (I) diazotised and treated with CuOH affords 8 : 8′-*dinitro*-1 : 1′-*dinaphthyl*, m.p. 295°, also obtained from (II) with Cu in boiling $PhNO_2$. (III) with Cu–$PhNO_2$ yields 4 : 8 : 4′ : 8′-*tetranitro*-1 : 1′-*dinaphthyl*, m.p. 260°. Similarly, diazotised 8 : 4 : 1-NO_2·$C_{10}H_5Br$·NH_2 with CuOH yields 4 : 4′-*dibromo*-8 : 8′-*dinitro*-1 : 1′-*dinaphthyl*, m.p. 294° (decomp.), also obtained from 4 : 1 : 8-$C_{10}H_5BrI$·NO_2 and Cu in boiling $PhNO_2$. (IV) diazotised and treated with CuOH yields 4 : 8 : 4′ : 8′-*tetranitro*-1 : 1′-*dinaphthylamine*, m.p. 244°. J. D. R.

Dissociable anthracene oxides : photo-oxides of *meso*-ditolylanthracenes. A. Willemart (Bull. Soc. chim., 1937, [v], **4**, 510—517).—Anthraquinone with *p*- or *m*-C_6H_4Me·MgBr gives 9 : 10-*dihydroxy*-9 : 10-*di*-p-, m.p. about 270° (block), and -m-*tolyl*-*anthracene*, m.p. 247—248° (block), reduced by KI–NaH_2PO_2–AcOH to 9 : 10-*di*-p-, m.p. 279°, and -m-*tolylanthracene*, m.p. 222° (block), which in light in CS_2 absorb 2O to give cryst. *photo-oxides*, which dissociate quantitatively when isolated. 9 : 10-*Di*-o-*tolylanthracene*, m.p. 347—348° (block), obtained from the 9 : 10-*diol*, m.p. 307—308° (block), absorbs O_2 much more slowly, but the product is also a dissociable photo-oxide. R. S. C.

Acenaphthene compounds.—See A., I, 307.

Action of sodamide and alkyl halides on *N*-arylformiminoethers. M. Grunfeld (Bull. Soc. chim., 1937, [v], **4**, 654—664).—Alkyl halides and the Na compounds formed from OEt·CH:NAr and $NaNH_2$ in C_6H_6 or PhMe give a mixture of equal proportions of HCO·NRAr and NAr:CH·NRAr together with some NHRAr and resinous products. Thus from OEt·CH:NPh and Bu^aBr are obtained *form*-n-*butylanilide*, b.p. 155—157°/18 mm. [synthesised from HCO·NHPh–$NaNH_2$–Bu^aBr; hydrolysed to give NHPhBu^a (NN′-*diphenyl*-N′-n-*butylcarbamide*, m.p. 68°)], and NN′-*diphenyl*-N′-n-*butylformamidine*, b.p. 189·5°/4 mm. (synthesised from NPh:CH·NHPh–$NaNH_2$–Bu^aBr), recognised by its hydrolysis products NH_2Ph and NHPhBu^a. Similarly using CH_2PhCl are obtained HCO·NPh·CH_2Ph and NN′-*diphenyl*-N′-*benzylformamidine*, b.p. 213—214°/2 mm. From *m*-C_6H_4Me·N:CH·OEt are obtained N-m-*tolyl*-N-*benzylformamidine*, m.p. 60—61° [hydrolysed to give

L (A., II.)

m-tolylbenzylamine (*hydrochloride*, m.p. 160—170°; *Bz* derivative, m.p. 69°)], and NN′-*di*-m-*tolyl*-N′-*benzylformamidine*, b.p. 224°/3 mm. [*hydrochloride*, m.p. 149—151°; *platinichloride*, m.p. 212—214° (decomp.)]. The NH_3 liberated in these reactions is < the theoretical quantity required for various suggested mechanisms. J. W. B.

Dissociation constants and rotations of some α-substituted ethylamines. J. M. Burch (Iowa State Coll. J. Sci., 1935, **10**, 55—57).—*sec.*-NH_2Bu, α-benzyl-, α-*p*-tolyl-, α-phenyl-, α-*p*-diphenyl-, and α-*o*-chlorobenzyl-ethylamine were resolved and the rotations of the pure amines, of their MeOH, EtOH, and C_6H_{14} solutions, and of the MeOH solutions of their hydrochlorides measured. The rotations of the α-substituted ethylamines were correlated with dissociation const. vals., with dipole moments, and with the nature of the substituent. Ch. Abs. (*e*)

Preparation of diphenyl-*p*-tolylamine and phenyldi-*p*-tolylamine. R. J. B. Marsden (J.C.S., 1937, 627).—$NHPh_2$ and $NH(C_6H_4Me)_2$ with *p*-C_6H_4MeI–K_2CO_3–Cu-bronze in boiling $PhNO_2$ afford, respectively, *diphenyl*-p-*tolylamine*, b.p. 230—244°/40 mm., m.p. 68·75° (corr.), and *phenyldi*-p-*tolylamine*, m.p. 109° (corr.). J. W. B.

Velocity of acetylation of aromatic aminosulphonic acids. A. I. Titov and A. N. Barischnikova (J. Gen. Chem. Russ., 1937, **7**, 357—362).—The velocity of acetylation of 1 : 6- and 1 : 7-NH_2·$C_{10}H_6$·SO_3H has been determined under different conditions. R. T.

Manufacture of acylated aromatic amines containing the trichloromethyl group.—See B., 1937, 327.

Manufacture of aromatic amines containing the trifluoromethyl group.—See B., 1937, 327.

Formation and decomposition of quaternary ammonium salts in solution.—See A., I, 313.

1 : 3-Diamino-1 : 2 : 2-trimethyl*cyclo*pentane. J. Suszko and F. Trzebniak (Rocz. Chem., 1937, **17**, 105—110).—1 : 3-Diamino-1 : 2 : 2-trimethyl-*cyclo*pentane, m.p. 141° (lit. 124°) (*carbonate*, +H_2O, m.p. 124°; *diurethane*, m.p. 173°), is prepared by hydrolysis of the corresponding 1 : 3-diazide, prepared from camphoric acid. R. T.

Complex salts of the racemic and optically active diamino*cyclo*hexanes with tervalent cobalt and rhodium. III. Tridiamino*cyclo*hexane salts of tervalent cobalt. F. M. Jaeger and L. Bijkerk (Proc. K. Akad. Wetensch. Amsterdam, 1937, **40**, 246—258; cf. A., I, 170).—When $CoCl_2,6H_2O$ (30 g.) dissolved in H_2O (110 c.c.) is mixed with *r*-, *d*-, or *l*-diamino*cyclo*hexane (Chxn) (27·5 g.) at 15° and 10% H_2O_2 (240 c.c.) is added slowly and with continuous shaking, a reddish-brown solution is obtained, which, after heating to remove excess of H_2O_2, addition of conc. HCl (450 c.c.), evaporation to dryness, and extraction with EtOH, yields a dark green hygroscopic mass of the *compound* $[Co(Chxn)_2Cl_2]Cl$ (I). On refluxing the *r*-form of (I) with theoretical amount of *r*-diamino*cyclo*hexane for 3 hr. the compound $[Co(r\text{-}Chxn)_3]Cl_3,H_2O$ (II)

is formed. The *compounds* $[Co(r\text{-Chxn})_3](NO_3)_3,3H_2O$ (III), $[Co(r\text{-Chxn})_3]Br_3,H_2O$ (IV), $[Co(r\text{-Chxn})_3](ClO_3)_3$ (V), and $[Co(r\text{-Chxn})_3](ClO_4)_3,3H_2O$) (VI) are also described. (II) can be resolved through the chloro-*d*-tartrates, the least sol. being the *compound* $L\text{-}[Co(d\text{-Chxn})_3]Cl(C_4H_4O_6),2H_2O$, and the most sol. the *compound* $D\text{-}[Co(l\text{-Chxn})_3]Cl(C_4H_4O_6),5H_2O$ (VIII). The crystal structures of (II)—(VIII) are described and the rotatory dispersion of (VII) and (VIII) have been investigated. J. W. S.

Constitution of compounds of cyclic diamines with metallic salts. R. Cernătescu, (Mme.) M. Papafil, and (Mlle.) M. Poni (Ann. Sci. Univ. Jassy, 1935, **20**, 175—189).—By determination of the wt. of (1) NH_3 fixed and (2) base (*B*) displaced when dry NH_3 is passed over the compounds of various metallic salts with diamines it is found whether each mol. of *B* is replaced by 1 mol. of NH_3 (*B* united by one valency) or by 2 (*B* united by two valencies). Thus $1:8\text{-}C_{10}H_6(NH_2)_2$ is united by one valency in $CdCl_2,2B$ and $CdBr_2,2B$, but by two valencies in $NiSO_4,2B$; in $CdBr_2,B$, *B* is united by one valency when it is 1 : 2-, and by two valencies when it is $1:5\text{-}C_{10}H_8(NH_2)_2$. With $p\text{-}C_6H_4(NH_2)_2$ the base is united by two valencies in $CdCl_2,B$, CdI_2,B (I), $Cd(NO_3)_2,2B$, and $NiCl_2,2B$, and also in $CdBr_2,p\text{-}C_6H_3Me(NH_2)_2$. Contrary to Hieber *et al.* (A., 1931, 412), ebullioscopic determination in C_5H_5N shows that (I) is a simple mol. and must, therefore, have the structure $C_6H_4(NH_2\ldots)_2MX_2$. J. W. B.

2 : 3-Diaminonaphthalene. H. Goldstein and M. Streuli (Helv. Chim. Acta, 1937, **20**, 520—524).—$2:3\text{-}C_{10}H_6(NH_2)_2$ (I) is conveniently obtained by heating $2:3\text{-}OH\cdot C_{10}H_6\cdot NH_2$ with $(NH_4)_2SO_3$–NH_3 at 170° in an enamelled autoclave. It gives a *picrate*, m.p. 210° (corr.), and a Bz_2 derivative, m.p. 271° (corr.). When heated with $1:2:4\text{-}C_6H_3Cl(NO_2)_2$ and cryst. NaOAc in EtOH (I) gives 3-*amino*-2-2′ : 4′-*dinitroanilinonaphthalene*, m.p. 200° (corr.). (I), NaOAc, and picryl chloride in EtOH at 60° give 3-*amino*-2-2′ : 4′ : 6′-*trinitroanilinonaphthalene*, m.p. 202° (corr.; decomp.), which is not cyclised when heated with $C_{10}H_8$ at 200—205°. With 2 : 4-dinitronaphthyl *p*-toluenesulphonate in EtOH at 100° (I) affords 3-*amino*-2-2′ : 4′-*dinitro*-1′-*naphthylaminonaphthalene*, m.p. 213° (corr.; decomp.), which does not lose HNO_2 in boiling $C_{10}H_8$ or quinoline. (I) is converted by boiling HCO_2H into lin.-*naphthiminazole*, m.p. 218° (corr.), and by boiling AcOH into 2-*methyl*lin.-*naphthiminazole*, m.p. 285° (corr.). (I), PhN_2Cl and NaOAc afford 2 : 3-*diamino*-1 : 4-*dibenzeneazonaphthalene*, from which $1:2:3:4\text{-}C_{10}H_4(NH_2)_4$ could not be obtained. H. W.

Regularities of colour indicators. H. Eichler (Monatsh., 1937, **70**, 79—83).—The groups responsible for the indicator colour changes in $p\text{-}NH_2\cdot C_6H_4\cdot N{:}NPh$ and in $p\text{-}OH\cdot C_6H_4\cdot N{:}NPh$ show their characteristic colour changes at the same p_H vals. in 4-amino-4′-hydroxyazobenzene (*hydrochloride*; *nitrate*) which is red in acid and yellow in alkaline solution. At p_H where no salt formation occurs either with NH_2 or OH the pale yellow neutral compound tends to be pptd. J. W. B.

Action of hydrazine and methylhydrazine on 1 : 5-dichloro-2 : 4-dinitrobenzene and derivatives of the compounds obtained. (Miss) J. L. Robert (Rec. trav. chim., 1937, **56**, 413—436).—5-Chloro-2 : 4-dinitrophenylhydrazine (A., 1921, i, 461) with boiling aq. EtOH containing $CuSO_4$ affords $1:2:4\text{-}C_6H_3Cl(NO_2)_2$ and with aldehydes and ketones in boiling EtOH containing H_2SO_4 affords the corresponding hydrazones. 5-*Chloro*-2 : 4-*dinitrophenylhydrazones* [m.p. (block) in parentheses] of the following aldehydes and ketones are prepared: MeCHO (192°); $COEt_2$ (108°); Me hexyl ketone (76°); heptaldehyde (108°); COPhMe (213°); *o*- (193° and 213°), *m*- (286°), and $p\text{-}C_6H_4Cl\cdot CHO$ (282°); *o*- (231° and 237°), *m*- (263°), and $p\text{-}NO_2\cdot C_6H_4\cdot CHO$ (335°); $p\text{-}OH\cdot C_6H_4\cdot CHO$ (275° and 281°); $p\text{-}OMe\cdot C_6H_4\cdot CHO$ (237°); $p\text{-}C_6H_4Me\cdot CHO$ (227° and 247°); $p\text{-}C_6H_4Pr^{\beta}\cdot CHO$ (213° and 225°); *o*-$OH\cdot C_6H_4\cdot CHO$ (290°); 4-hydroxy-3-methoxybenzaldehyde (266°); 3 : 4-methylenedioxybenzaldehyde (247°); furfuraldehyde (234°); 5-methyl- (202°) and 5-hydroxymethyl-furfuraldehyde (208°). $NHMe\cdot NH_2$ with 1 : 5-dichloro-2 : 4-dinitrobenzene (I) in boiling EtOH affords 5-*chloro*-2 : 4-*dinitrophenylmethylhydrazine* (II), m.p. 183° (block) [*Ac* derivative, m.p. 186° (block) and 197° after resolidifying], which with $CuSO_4$ in boiling aq. EtOH gives 5-chloro-2 : 4-dinitromethylaniline, m.p. 161—163° (lit., 106—107°). 5-*Chloro*-2 : 4-*dinitrophenylmethylhydrazones* [m.p. (block) in parentheses] of the following aldehydes and ketones are described: CH_2O (152°); MeCHO (200°); $COMe_2$ (192°); $COEt_2$ (90°); Me hexyl ketone (55—58°); $CH_2Ac\cdot CO_2Et$ [127° (Thiele)]; heptaldehyde (45—46°); COPhMe [143° (Thiele)]; PhCHO (197°); *o*- (176°), *m*- (196°), and $p\text{-}C_6H_4Cl\cdot CHO$ (206° and 219°); *o*- (222°), *m*- (239°), and $p\text{-}NO_2\cdot C_6H_4\cdot CHO$ (279°); $p\text{-}OH\cdot C_6H_4\cdot CHO$ (197°, 205°, and 215°); $o\text{-}OH\cdot C_6H_4\cdot CHO$ (237°); $p\text{-}OMe\cdot C_6H_4\cdot CHO$ (227°); $p\text{-}C_6H_4Me\cdot CHO$ (219°); $p\text{-}C_6H_4Pr^{\beta}\cdot CHO$ (154° and 163°); 4-hydroxy-3-methoxy- (217°) and 3 : 4-methylenedioxy-benzaldehyde (214°); furfuraldehyde (205°); 5-methyl- (132° and 173°) and 5-hydroxymethyl-furfuraldehyde (108°). $NHMe\cdot NH_2$ with (I) in boiling EtOH affords (II) and 2 : 4-*dinitro*-1 : 5-*di*-(α-*methylhydrazino*)*benzene* (III), m.p. 270° (block) [*Ac* derivative, m.p. 350° (block)] (cf. *loc. cit.*), which with $FeCl_3$ in boiling EtOH affords 2 : 4-dinitrophenylene-1 : 3-dimethylamine (cf. A., 1902, i, 715). (III) reacts as above with the following ketones and aldehydes to give 2 : 4-*dinitrophenylene*-1 : 5-*di*-α-*methylhydrazones* [m.p. (block) in parentheses]: CH_2O (150° and 163°); COPhMe (206°); PhCHO (236°); $o\text{-}OH\cdot C_6H_4\cdot CHO$ (245°); furfuraldehyde (106°, 203°, and 213°); and 4 : 6-dinitro-1 : 3-di-(α-methyl-β-acetylhydrazino)benzene (305°). Similarly, 2 : 4-*dinitrophenylene*-1 : 5-*dihydrazones* of the following are prepared: COPhMe (270°); $o\text{-}OH\cdot C_6H_4\cdot CHO$ (324°); and furfuraldehyde (293°). (II) with N_2H_4,H_2O in boiling EtOH affords 2 : 4-*dinitro*-1-*hydrazino*-5-(α-*methylhydrazino*)*benzene*, m.p. 193—194° (block) [Ac_2 derivative (IV), m.p. 268° and 283° (block)] (obtained in 4 cryst. forms), which gives with $CuSO_4$, $FeCl_3$, and HgO unidentified oxidation products and reacts with the following aldehydes and ketones to give *dihydrazones* [m.p.

(block) in parentheses]: CH_2O (190°); MeCHO (178°); $COMe_2$ (147°); $COEt_2$ [110—112° (Thiele)]; Me hexyl ketone (86°); heptaldehyde (95°); COPhMe (201°); PhCHO (243°); *o*- (236°), *m*- (206° and 231°), and *p*-C_6H_4Cl·CHO (271°); *o*- (246° and 256°), *m*- (280°), and *p*-NO_2·C_6H_4·CHO (325°); *p*-OH·C_6H_4·CHO (205° and 290°); *o*-OH·C_6H_4·CHO (281°); *p*-OMe·C_6H_4·CHO (248°); *p*-C_6H_4Me·CHO (222° and 248°); *p*-$C_6H_4Pr^{\beta}$·CHO (241° and 354°); vanillin (201° and 242°); piperonaldehyde (200° and 267°); furfuraldehyde (256°); 5-methyl- (190° and 223°) and 5-hydroxymethyl-furfuraldehyde (decomp. 223°); (IV) (268° and 283°); and the 2 : 4-dinitro-5-(α-methylhydrazino)phenylhydrazone [172° (V)] of $CH_2Ac·CO_2Et$. 5-Chloro-2 : 4-dinitrophenylhydrazine with $CH_2Ac·CO_2Et$ in boiling EtOH containing H_2SO_4 affords the 5-chloro-2 : 4-dinitrophenylhydrazone of $CH_2Ac·CO_2Et$, which with the calc. amount of $NHMe·NH_2$ in boiling EtOH affords (V). J. L. D.

Connexion between complex formation and redox reactions. I. L. Kulberg (J. Gen. Chem. Russ., 1937, **7**, 381—387).—Oxidation of org. compounds by $Ag^{\cdot}$ depends not only on the E_0 of the compound, but also on whether complex formation with $Ag^{\cdot}$ takes place. This is shown to be the case for a series of phenols, aminophenols, and $CHPh_3$ dyes. R. T.

Effect of substituents on the germicidal activity of phenols. I. **Alkyl derivatives of 2 : 4-dibromophenol.** S. L. Chien, H. P. Chung, and H. C. Tai (J. Chinese Chem. Soc., 1936, **4**, 361—369).—2 : 4-$C_6H_3Br_2$·OH and 3 : 5-dibromo-*o*-cresol are prepared in 86 and 95% yield, respectively. The following are obtained by acylation of the phenol, Fries rearrangement, and Clemmensen reduction. 2 : 4-*Dibromophenyl* acetate, m.p. 36°, propionate, b.p. 145—146°/15 mm., *butyrate*, b.p. 178—181°/20 mm., and *valerate*, b.p. 153—154°/1 mm. 3 : 5-*Dibromo*-2-*hydroxy*-*aceto*-, m.p. 109—110°, -*propio*-, m.p. 116·5—117°, -*butyro*-, m.p. 71—72°, and -*valerophenone*, m.p. 74·5—76°. 2 : 4-*Dibromo*-6-*ethyl*-, b.p. 121—122°/3·5 mm., -n-*propyl*-, b.p. 130—131°/4·5 mm., -n-*butyl*-, b.p. 139—141°/2 mm., and -n-*amylphenol*, b.p. 159—161°/4 mm. R. S. C.

New aromatic fluoro-derivatives. A. C. de Degiorgi and E. V. Zappi (Anal. Asoc. Quím. Argentina, 1936, **24**, 119—130).—3-Fluoro-5-nitroanisole (I) (A., 1936, 1374) with Sn and HCl gives 3-*fluoro*-5-*aminoanisole*, a liquid (*sulphate*; *dihydrate*) which on diazotisation and decomp. in presence of $NaNO_2$ gives (I), and with HCl for 5 hr. at 170—180° yields 3-*fluoro*-5-*nitrophenol* (II), m.p. 112°, which on methylation gives (I). Diazotised 3-nitro-5-aminophenetole with 40% HBF_4 gives 3-*nitrophenetole*-5-*diazonium borofluoride*, decomp. 110°, which loses BF_3 at 110° to yield 3-*fluoro*-5-*nitrophenetole*, m.p. 63·5—64°, hydrolysed to (II). 1 : 3 : 5-$C_6H_3F(NO_2)_2$ with 1 mol. of $(NH_4)_2S$ in aq. EtOH yields 3-*fluoro*-5-*nitroaniline*, m.p. 115—116°, which by diazotisation and subsequent decomp. yields *m*-$C_6H_4F·NO_2$. F. R. G.

Cleavage of diphenyl ethers by sodium in liquid ammonia. I. ***o*- and *p*-Substituted diphenyl ethers.** P. A. Sartoretto and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 603—606).—By determination of the cleavage products produced from substituted Ph_2 ethers by Na in liquid NH_3 the following are found to increase the strength of the Ph·O linking: *o*- < *p*-Me < *p*-OMe < *o*- < *p*-NH_2, whilst the following decrease it: *o*-OMe < *o*- < *p*-CO_2Na. Thus, the tautomeric effect dominates the inductive effect, except for *o*-OMe. *Ph* p-, b.p. 200°/15 mm., m.p. 56—58°, and o-*nitro*-, b.p. 185°/8 mm., p-, b.p. 188°/14 mm., m.p. 83·5°, and o-*amino*-, b.p. 170°/18 mm., m.p. 44°, o-, m.p. 112—114°, and p-*carboxy*-*phenyl ether*, m.p. 141°, *Ph* o-, b.p. 101°/5 mm., and p-*tolyl*, b.p. 114°/6 mm., o-, b.p. 288°/745 mm., m.p. 76°, and p-*anisyl ether*, b.p. 125°/5 mm., o-*tolyl* p-*tolyl ether*, b.p. 121°/7 mm., and o-*anisyl* p-*anisyl ether*, b.p. 203°/20 mm., m.p. 77°, are described. R. S. C.

Iodination of phenols. C. V. Bordeianu (Ann. Sci. Univ. Jassy, 1935, **20**, 131—138).—Iodination of phenols is readily effected (*a*) with I–MeOH and the phenol in MeOH–NH_3, or (*b*) by addition of ·HgAc derivatives in alkaline solution to I–AcOH. Thus are prepared (*a*) iodo-*o*-xylenol and the I_2-derivative, m.p. 176—177° (decomp.) (*Ac* derivative, m.p. 153—154°), of *m*-5-xylenol, and (*b*) 2 : 6-*di*-*iodo*-3-*hydroxy*-p-*xylene*, m.p. 63°. 6-*Bromo*-2-*iodothymol* was obtained by method (*b*). J. W. B.

Colour of 2-nitrodiphenylamine-4-arsinic acid derivatives, containing additional auxo-groups. II. **Colour of nitrobenzoyl derivatives of aromatic amines.** III. **Influence of position of nitro- and auxo-groups on colour of nitrobenzoylarylamines.** V. A. Ismailski and E. A. Smirnov (J. Gen. Chem. Russ., 1937, **7**, 513—522, 523—537; cf. this vol., 267).—II. The CO·NH group is shown to act as a chromophore in a no. of *m*- and *p*-nitrobenzoyl derivatives of substituted anilines, the intensity of coloration depending on the nature and position of the auxochrome groups. The N-p-*nitrobenzoyl* derivatives of m-*aminophenol*, m.p. 212°, p-*anisidine*, m.p. 197°, m-, m.p. 188°, and p-*dimethylaminoaniline*, m.p. 258·5°, and the m-*nitrobenzoyl* derivatives of m-*aminophenol*, m.p. 219°, p-*anisidine*, m.p. 174·5°, p-N-*methylaminophenol*, m.p. 224°, m-, m.p. 176°, and p-*dimethylaminoaniline*, m.p. 173°, are described.

III. The absorption spectra of the above compounds are given, and the causes of differences in absorption for *m*- and *p*-substituted compounds are discussed. R. T.

Derivatives of 3-amino-2-naphthol. H. Goldstein and P. Gardiol [with M. Comtesse, R. Mohr, and H. Fischer] (Helv. Chim. Acta, 1937, **20**, 516—520).—2 : 3-OH·$C_{10}H_6$·NH_2 (I) gives a *picrate*, m.p. 206° (decomp.). (I) is transformed by boiling 90% HCO_2H into 3-*formamido*-2-*naphthol*, m.p. 193° (corr.), and by cold Ac_2O into 3-*acetamido*-2-*naphthol*, m.p. 244° (corr.). 2 : 3-OH·$C_{10}H_6$·NHBz is converted by BzCl and NaOH at 100° into its *benzoate*, m.p. 184° (corr.), and by boiling Ac_2O into the corresponding *acetate*, m.p. 154° (corr.). (I) yields a very unstable diazo-compound from which 3 : 2-$C_{10}H_6I$·OH, m.p. 105° (corr.), is obtained in poor yield. (I) couples with *p*-$SO_3H·C_6H_4·N_2Cl$ in alkaline solution and the

resulting compound is reduced by $SnCl_2$ and HCl to 1 : 3-*diamino*-2-*naphthol* [*dihydrochloride*; Ac_3 derivative, m.p. 239° (corr.)]. Similar coupling in acid solution followed by reduction leads to 3 : 4-*diamino*-2-*naphthol dihydrochloride*. (I) is converted by PhI, K_2CO_3, and Cu powder in boiling PhMe into 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}NHPh$, m.p. 131° (corr.). H. W.

Syntheses in the phenanthrene series. VI. 3-Methoxy-1-methylphenanthrene. P. Hill, W. F. Short, H. Stromberg, and A. E. Wiles (J.C.S., 1937, 510—513).—The Mg compound (I) of 6-bromo-*m*-tolyl Me ether with β-chloroethyl *p*-toluenesulphonate in C_6H_6 gives β-(5-*methoxy*-o-*tolyl*)*ethyl chloride*, b.p. 134—135°/10 mm., the Mg compound of which with *cyclo*hexanone gives αδ-*di*-(5-*methoxy*-o-*tolyl*)-*butane*, m.p. 87°, and the crude *cyclo*hexanol, dehydrated by $KHSO_4$ at 165° to 1-β-(5′-*methoxy*-o-*tolyl*)-*ethyl*-Δ^1-*cyclohexene*, b.p. 192—195°/18 mm. This with $AlCl_3$ in CS_2 at 0°—room temp. and dehydrogenation of the product with S at 180—240° gives 3-*methoxy*-1-*methylphenanthrene* (II), m.p. 90° [*picrate* (III), m.p. 147°]. (I) and $CH_2{:}CH{\cdot}CH_2Br$ give 6-*allyl*-m-*tolyl Me ether*, b.p. 107—108°/10 mm., oxidised by 5% $KMnO_4$–aq. AcOH at <0° to 5-*methoxy*-o-*tolylacetic acid*, m.p. 106·5—107°, the K salt of which with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ in Ac_2O at 100° gives 2-*nitro*-, m.p. 169·5—170°, reduced by $FeSO_4$–aq. NH_3 to the (unstable) 2-*amino*-α-(5′-*methoxy*-o-*tolyl*)-*cinnamic acid*, m.p. 171—172°, diazotisation of which affords 3-*methoxy*-1-*methylphenanthrene*-10-*carboxylic acid*, m.p. 199—200°, decarboxylated by Cu powder in quinoline at 230° to (II). Demethylation of (II) with HI (*d* 1·7)–AcOH affords 3-*hydroxy*-1-*methylphenanthrene* (IV), m.p. 161°. This couples with diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2H$ to give a red dye, reductive fission of which with $Na_2S_2O_4$ gives an unstable NH_2-phenol, oxidised by CrO_3–AcOH at 0° to 1-*methylphenanthra*-3 : 4-*quinone*, decomp. 300°, converted by Zn–Ac_2O–C_5H_5N into 3 : 4-*diacetoxy*-1-*methylphenanthrene*, m.p. 138·5—139°. The m.p. of (II), (III), and (IV) are depressed by admixture with the isomeric compounds obtained by dehydrogenation of podocarpic acid. J. W. B.

Synthesis of halogenated thiocresols. S. L. Chien and H. T. Kuan (J. Chinese Chem. Soc., 1936, 4, 355—360).—*o*-Toluidine-5-sulphonic acid affords (diazo-reaction) 2-bromotoluene-5-sulphonic acid, the chloride of which with Sn–HCl gives 6-bromo-*m*-thiocresol, m.p. 80—81° (lit. an oil). Similarly are prepared 4-*bromo*-o-, b.p. 107—108°/2 mm., 4-*chloro*-*o*-, m.p. 80—81°, and -*m*-*thiocresol*, m.p. 67—68°, and 4-*chlorotoluene*-2-, m.p. 24°, and -3-*sulphonyl chloride*, m.p. 50°. R. S. C.

Reaction between thallium chloride and bromide and certain phenols. N. N. Melnikov and G. P. Gratscheva (J. Gen. Chem. Russ., 1937, 7, 467—469).—$TlCl_3$ or $TlBr_3$ and α- or β-$C_{10}H_7{\cdot}OH$ in H_2O yield *thallium tri*-α-, m.p. 74—78°, and *tri*-β-*naphthoxide*, m.p. 109—112°. *o*-, *m*-, and *p*-$C_6H_4(OH)_2$ are oxidised by $TlCl_3$, with production of quinones and TlCl. Phloroglucinol yields a highly toxic additive *compound*, $C_6H_3(OH)_3{,}TlBr_3$, decomp. at 200°. R. T.

Pharmacologically active compounds from β-alkoxyphenylethylamines. W. S. Ide and J. S. Buck (J. Amer. Chem. Soc., 1937, 59, 726—731).—The following are prepared by methods previously described, starting from the appropriate phenolic aldehydes. 3 : 4-*Diethoxycinnamic acid*, m.p. 156°. γ-3-*Methoxy*-2-*ethoxyphenylpropionic acid*, m.p. 65° (*amide*, m.p. 85°). γ-o-, m.p. 106°, -m-, m.p. 80°, and -p-*Ethoxyphenylpropionamide*, m.p. 137°. β-o-, b.p. 128—130°/13 mm. (hydrochloride, m.p. 218°; p-*nitrobenzoyl* derivative, m.p. 120°), -m-, b.p. 135—138°/13 mm. (*hydrochloride*, m.p. 168°, gels at 146°; p-*nitrobenzoyl* derivative, m.p. 113°), and -p-*ethoxy*-, b.p. 138—140°/3 mm. (*hydrochloride*, m.p. 206°; p-*nitrobenzoyl* derivative, m.p. 154°), -3-*methoxy*-2-*ethoxy*-, b.p. 148—150°/13 mm. (*hydrochloride*, m.p. 162°; p-*nitrobenzoyl* derivative, m.p. 102°), -3-*methoxy*-4-*ethoxy*-, b.p. 160°/13 mm. (*hydrochloride*, m.p. 168°; p-*nitrobenzoyl* derivative, m.p. 157°), -4-*methoxy*-3-*ethoxy*-, b.p. 168°/15 mm. (*hydrochloride*, m.p. 168°; p-*nitrobenzoyl* derivative, m.p. 156°), and -3 : 4-*diethoxy-phenylethylamine*, b.p. 158°/13 mm. [hydrochloride, new m.p. 198° (gels at 144°); p-*nitrobenzoyl* derivative, m.p. 138°]; the corresponding β-*phenylethylmethylamines*, b.p. 97°/2 mm., 106°/2 mm., 107°/2 mm., 119°/1·5 mm., 128°/1·5 mm., 129°/1·5 mm., and 129°/2 mm. (*hydriodides*, m.p. 118°, 74°, 129°, 122°, 228°, 154°, and 100°, respectively; *hydrochlorides*, m.p. 133°, 144°, 206°, 147°, 131°, 159°, and 157°; p-*nitrobenzoyl* derivatives, m.p. 235°, 222°, 118°, 78°, 155°, 102°, and 58°, respectively); the corresponding *phenylethylcarbamides*, m.p. 112°, 104°, 134°, 120°, 126°, 145°, and 108°, respectively; the corresponding as-*methylcarbamides*, m.p. 84°, 118°, 149°, 76°, 112°, 96°, and 97°, respectively; the corresponding 1-β-x-*alkoxyphenylethyl*-5 : 5-*diethylbarbituric acids*, m.p. 66°, 86°, 134°, 68°, 120°, 99°, and 88°, respectively; the corresponding N-*benzylamine hydrochlorides*, m.p. 122°, 194°, 240°, 162°, 200°, 195°, and 190°, respectively; the corresponding N-o′-*ethoxybenzylamine hydrochlorides*, m.p. 153°, 135°, 143°, 168°, 128°, 174°, and 168°, respectively; the corresponding N-m′-*ethoxybenzylamine hydrochlorides*, m.p. 113°, 146°, 167°, 124°, 106°, 103°, and 104°, respectively; the corresponding N-p′-*ethoxybenzylamine hydrochlorides*, m.p. 134°, 195°, 280°, 120°, 239°, 218°, and 208°, respectively; the corresponding N-3′ : 4′-*diethoxybenzylamine hydrochlorides*, m.p. 148°, 114°, 186°, 113°, 154°, 122°, and 112°, respectively. β-o-*Ethoxyphenylethyl*-N-o′-*ethoxybenzylamine*, m.p. 133°. β-3-*Methoxy*-4-*ethoxy*-, m.p. 78°, and -3 : 4-*diethoxy-phenylethyl*-N-p′-*ethoxybenzylamine*, m.p. 105°. β-3-*Methoxy*-4-*ethoxy*-, m.p. 92°, and -3 : 4-*diethoxy-phenylethyl*-N-3′ : 4′-*diethoxybenzylamine*, m.p. 98°. p′-*Ethoxy*-, m.p. 90°, and 3′ : 4′-*diethoxy-benzylidene*-β-p-*ethoxyphenylethylamine*, m.p. 86°; *benzylidene*-, m.p. 67°, p′-*ethoxy*-, m.p. 107°, and 3′ : 4′-*diethoxy-benzylidene*-β-3-*methoxy*-4-*ethoxyphenylethylamine*, m.p. 115°; o′-, m.p. 66°, and p′-*ethoxy*-, m.p. 60°, and 3′ : 4′-*diethoxy-benzylidene*-β-4-*methoxy*-3-*ethoxyphenylethylamine*, m.p. 96°; o′-, m.p. 52°, and p′-*ethoxy*-, m.p. 96°, and 3′ : 4′-*diethoxy-benzylidene*-β-3 : 4 - *diethoxyphenylethylamine*, m.p. 122°. 6-*Ethoxy*-, m.p. 251° [N-*Me* derivative (*hydrochloride*, froths at 144°, decomp. 220°)], 6-

methoxy-5-*ethoxy*-, m.p. 184° [N-*Me* derivative (*hydrochloride*, m.p. 220°)], 6-*methoxy*-7-*ethoxy*-, m.p. 284° [N-*Me* derivative (*hydrochloride*, m.p. 270°)], 7-*methoxy*-6-*ethoxy*-, m.p. 282° [N-*Me* derivative, (*hydrochloride*, m.p. 208°)], and 6 : 7-*diethoxy*-1 : 2 : 3 : 4-*tetrahydroisoquinoline hydrochloride*, m.p. 268° [N-*Me* derivative (*hydrochloride*, m.p. 198°)].

R. S. C.

Synthesis of long-chain substituted isocyclics and similarly substituted adipic acids. (A) **Preparation of 4-*tert*.-octyl*cyclo*-hexanol, -hexene, -hexanone, -hexyl-hydroxylamine, -amine, and -phenol, and β-*tert*.-octyladipic acid.** J. B. Niederl and R. A. Smith. (B) **Preparation of 2-*tert*.-octyl*cyclo*hexanone. Method of indirect proof of structure for *o*- and *p*-alkylphenols.** J. B. Niederl and J. B. Whitman (J. Amer. Chem. Soc., 1937, **59**, 715—717, 717—718).—(A) 4-αα*γγ*-*Tetramethylbutyl*cyclo*hexanol* (I) (prep. by hydrogenation of "*p*-di*iso*butylphenol"), b.p. 148—150°/11·5 mm., m.p. 55·5—56°, with a little H_2SO_4 at 130—140° gives αα*γγ*-*tetramethylbutyl*-Δ³-cyclo*hexene* (II), b.p. 113°/12 mm., and with $K_2Cr_2O_7$ gives 4-αα*γγ*-*tetramethylbutyl*cyclo*hexanone* (III), b.p. 142—144°/11 mm. (*NaHSO*$_3$ compound). (II), PhOH, and H_2SO_4 at 60° give p-4′-αα*γγ*-*tetramethylbutyl*-cyclo*hexylphenol*, m.p. 81°, b.p. 110—120°/2 mm. The *oxime*, m.p. 152°, of (III) with H_2–Ni in 95% EtOH at 3·3 atm. yields 4-αα*γγ*-*tetramethylbutyl*cyclo-*hexylhydroxylamine hydrochloride*, m.p. 240—245° (decomp.), and thence by Na–EtOH the *amine hydrochloride*, m.p. 260—265° (decomp.). (I), (II), or (III) with 50% HNO_3 and, best, a trace of V_2O_5 at 110° gives 60% of β-α′α′γ′γ′-*tetramethylbutyladipic acid*, m.p. 133—134°.

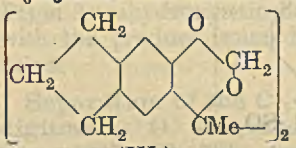
(B) *o*- and *p*-Alkylphenols can be differentiated by reduction to the *cyclo*hexanol and oxidation; the former give adipic acid, the latter a β-substituted adipic acid. For comparison the *o*-alkylphenol can be obtained from *cyclo*hexanone, $NaNH_2$, and the alkyl bromide. 2-αα*γγ*-*Tetramethylbutyl*cyclo*hexanone*, b.p. 140—144°/11 mm. (*oxime*, m.p. 147—148°), is thus obtained in 16% yield and oxidised.

R. S. C.

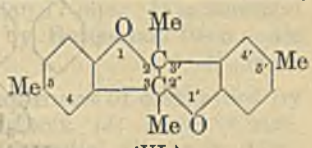
Preparation of diastereoisomeric pairs of alcohols. P. Jullien and F. Kayser (Bull. Soc. chim., 1937, [v], **4**, 700—711).—Contrary to the behaviour of MgPhBr (A., 1936, 1375), MgEtBr, MgBu^{a}Br, and CH_2Ph·MgCl react with aldehydes to give a mixture of the two diastereoisomerides. Thus CHPhEt·CHO and MgEtBr in dry Et_2O give a mixture of (α)-, m.p. 47·5° (*phenylurethane*, m.p. 109°) and (β)-*γ*-*phenylhexan*-δ-*ol*, b.p. 119—121°/15 mm. (*phenylurethane*, m.p. 127°); with MgBu^{a}Br are obtained (α)-, m.p. 51°, and (β)-*γ*-*phenyl*-n-*octan*-δ-*ol*, b.p. 148—151°/17 mm. (*phenylurethane*, m.p. 106°), and CH_2Ph·MgCl affords a mixture of (α)-, m.p. 140° (*phenylurethane*, m.p. 65°), and (β)-α*γ*-*diphenyl*-n-*pentan*-β-*ol*, m.p. 77° (*phenylurethane*, m.p. 94°). From the products of the action of CH_2Ph·MgCl with CHMePh·CHO only (β)-α*γ*-*diphenyl*-n-*butan*-α-*ol*, m.p. 76° (*phenylurethane*, m.p. 90—91·5°), is isolated. The β-forms of these alcohols are the sole products obtained by reduction of the corresponding ketones with Na–EtOH. The ketones were prepared by the action of the appropriate MgRX on CHEtPh·CO·NH_2 or CHEtPh·CN and thus is obtained α-*phenyl*-n-*propyl Bu^a ketone*, b.p. 133—134°/14 mm. (*semicarbazone*, m.p. 99°); prepared by various methods CHEtPh·CO·CH_2Ph has b.p. 187—189°/17 mm. (semicarbazone, m.p. 143°). J. W. B.

Molecular rearrangements during the dehydration of 4-methyl*cyclo*hexyl*iso*propylpinacol. M. Godchot and (Mlle.) G. Cauquil (Compt. rend., 1937, **204**, 733—736).—Me 4-methyl*cyclo*hexan-1-ol-1-carboxylate (this vol., 149) with MgMeI affords 1-(β-*hydroxyiso*propyl)-4-*methyl*cyclo*hexanol*, m.p. 95—96°, dehydrated by aq. $H_2C_2O_4$ at 120° to a mixture of 1-methyl-4-*iso*propenyl-Δ³-*cyclo*hexene (60%) (Raman spectrum determined), 2 : 2 : 5-*trimethyl*-cyclo*heptanone* (4%), b.p. 86—87°/12 mm. (*semicarbazone*, m.p. 200—201°; *oxime*, m.p. 62°), and 1 : 4-*dimethyl*cyclo*hexyl Me ketone* (36%), b.p. 85°/12 mm. (*semicarbazone*, m.p. 156°; *oxime*, m.p. 123°), oxidised by NaOBr at 70° to $CHBr_3$ and 1 : 4-*dimethyl*-cyclo*hexane*-1-*carboxylic acid*, b.p. 135°/14 mm. (*amide*, m.p. 127—128°). J. W. B.

Pinacols derived from *o*-hydroxyacetophenones. W. Baker and J. C. McGowan (J.C.S., 1937, 559—562).—Reduction of 5-hydroxy-6-acetylhydrindene [5-O-*Ac* derivative (I), m.p. 88°] with Zn dust —4% aq. NaOH gives 6-(5-*hydroxyhydrindyl*)*methylpinacol* (II), m.p. 122°, converted by Ac_2O into (I). (II) in aq. $COMe_2$—10% KOH with CH_2SO_4 affords 4 : 4′-*bis*-(4-*methyl*-6 : 7-*trimethylene*-1 : 3-*benzdioxinyl*) (III), m.p. 172°. Similar reduction of 1 : 3 : 4-C_6H_3MeAc·OH affords a mixture of stereoisomerides,



(III.)

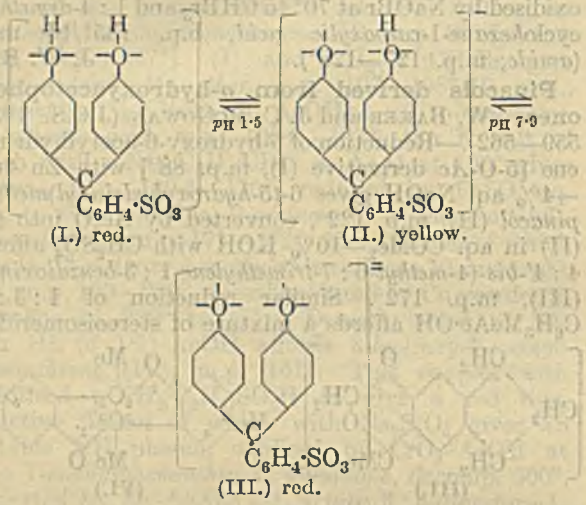


(VI.)

separated by boiling EtOH into the α- (? dl) (IV), m.p. 273° (decomp.) (less sol., 20% yield), and β- (? meso)-4-*hydroxy*-m-*tolylmethylpinacol* (V), m.p. 170° (decomp.) (from the mother-liquor; 60% yield). When heated in glacial AcOH the α-compound is converted into α-2 : 3 : 5 : 5′-*tetramethylcoumarano*-3′ : 2′ : 2 : 3-*coumaran* (VI), m.p. 151°, but the β-compound with boiling HCl–EtOH gives a mixture of (VI) and (?) a stereoisomeride of higher m.p. Methylenation of (IV) and (V) gives, respectively, α-, m.p. 243°, and β-4 : 4′-*bis*-(4 : 6-*dimethyl*-1 : 3-*benzdioxinyl*), m.p. 134—135°. J. W. B.

Molecular resonance systems. I. General. G. Schwarzenbach, M. Brandenberger, G. H. Ott, and O. Hagger. **II. Preparation and properties of substituted anilinesulphonephthaleins.** G. Schwarzenbach, G. H. Ott, and O. Hagger (Helv. Chim. Acta, 1937, **20**, 490—498, 498—513).—I. Resonance systems are defined as mols. in which two or more types of electron distribution are possible. The ionised carboxyl represents a symmetrical system $O{=}CR{-}O^- \rightleftharpoons {-}O{-}CR{=}O$ whereas CO_2H is an unsymmetrical system $O{=}CR{-}O{-}H \rightleftharpoons {-}O{-}CR{=}O{-}H$. Such simple resonance systems

are formed particularly by C and N. They are readily studied with dyes in which the absorption of light is intimately connected with the resonance. In them a large no. of π electrons is distributed over the whole or greater part of the mol. in such a manner that independent oscillation is excluded, thus causing absorption in the region of longer λ. Dyes are resonance systems in which two or more groups with free pairs of electrons (auxochromes) are united to an unsaturated C skeleton (chromophor) in such a manner that double linkings can be displaced without considerable modification of the stability of the mol. The acidity relationships of dyes with two-sided resonance systems are investigated with respect to phenolsulphonephthalein (I) (phenol-red). Removal of the first proton transforms the symmetrical into the unsymmetrical resonance (II), whilst departure of the second proton leads to the symmetrical form. Since resonance is causative of colour it is



immediately obvious that dissociation is accompanied by colour change. In consequence of the longer resonance chains the symmetrical forms invariably absorb in regions of longer λ than the unsymmetrical forms. With regard to acidity, the free electron pairs of the auxochromes can participate in the resonance or be impeded by a proton. The tendency of such a pair to add a proton is less on account of the resonance demand, which has a very marked influence. The dissociation consts. of such indicators are therefore governed by the normal acidity of the acidic group and the difference in energy of the two resonance systems which pass into one another. The stepwise dissociation of (I) is conditioned not only by the charge remaining on the mol. after loss of the first proton but also electronically. The new $-\overset{|}{O}-$ group formed by loss of the first proton is a much better source of electrons for the central C than is the residual OH. The unsymmetrical resonance of (II) is very similar to that of a quinone. Almost the complete electron pair is provided from the one side. Discharge of the remaining OH by resonance causes diminution of its acidity. The dissociation stages of amilinesulphonephthalein are precisely similar to those of (I). Consideration of similar dyes shows increasing stability of the resonance system in the following series of auxochromes: $F\text{-}\overset{|}{N}H_3$, $F\text{-}\overset{|}{O}H$, $F\text{-}\overset{|}{O}Me$, $F\text{-}\overset{|}{N}H_2$, $F\text{-}\overset{|}{O}\text{-}$, $F\text{-}\overset{|}{N}H$ (F = dye]. Annihilation of the resonance system occurs when the central atom does not receive sufficient electrons from the auxochromes and is obliged to satisfy its demand from outside the mol. Such electrons are commonly acquired from OH′ present in aq. solutions [conversion of $CPh(C_6H_4X)_2$ into $OH\cdot CPh(C_6H_4X)_2$] or from CN′, SO_3H′, or H·.

II. (I) when heated with the substituted aniline at about 200° is transformed into substituted *anilinesulphonephthaleins*, $SO_3\cdot C_6H_4\cdot C(C_6H_4\cdot NHR)_2$, in which R = o-*tolyl*, 2 : 4-*dimethylphenyl*, 2 : 4 : 5-*trimethylphenyl*, p-*anisyl*, and p-*ethoxyphenyl*. The *compounds* in which R = H, Me, or Et are derived similarly with NH_3 and primary aliphatic amines. Very protracted heating leads to production of the corresponding leuco-compounds. Attempts to obtain chlorobenzenesulphonephthalein from PhCl and $o\text{-}C_6H_4\langle^{SO_2}_{CO}\rangle O$ were unsuccessful, whilst the interaction of (I) and PCl_5 gives non-homogeneous phosphoric esters transformed by a small excess of the requisite amine in EtOH at 100° into *anilinesulphonephthaleins* in which R = Pr$^{\alpha}$, Bu$^{\beta}$, $OH\cdot CH_2\cdot CH_2\cdot$, $\cdot CH_2Ph$, $p\text{-}OH\cdot C_6H_4\cdot$, $m\text{-}OH\cdot C_6H_4\cdot$, $p\text{-}NH_2\cdot C_6H_4\cdot$, and $o\text{-}C_6H_4Br\cdot$. The Ac_2 derivative of (I) with a large excess of the requisite amine in EtOH at 100° yields *anilinesulphonephthaleins* in which R = $2:4\text{-}C_6H_3Cl_2\cdot$, $m\text{-}C_6H_4Ac\cdot$, $C_6H_4Ph\cdot$, $NHBz\cdot$, $NMe_2\cdot$, $NEt_2\cdot C_2H_4\cdot$, $CO_2Et\cdot CH_2\cdot$, $CO_2H\cdot CH_2\cdot$. In the first two methods condensation proceeds in two distinct stages but the primary product is exceedingly reactive and could not be isolated. In all three methods N_2H_4 and $NHPh\cdot NH_2$ behave solely as reducing agents. The dyes are generally cryst., very sparingly sol. in H_2O, freely sol. in EtOH. All have indicator nature which is fully discussed from the viewpoint of Part I. They are readily brominated in AcOH (*tetrabromo-* and *tetrabromo-N-ethyl-anilinesulphonephthalein*). They give freely sol. sulphonic acids (amorphous *Ba* and *Ca* salts) which are non-homogeneous. H. W.

Constituents of plant seedlings. I. New compounds from the unsaponifiable matter of wheat-germ oil. P. Karrer and H. Solomon (Helv. Chim. Acta, 1937, **20**, 424—436).—Sitosterols are removed as far as possible by treatment of the unsaponifiable matter with MeOH and the residue is analysed chromatographically (Al_2O_3), thereby giving results closely similar to those of Drummond *et al.* (A., 1935, 418, 1551). The materials in layer *C* (probably corresponding with vitamin-*E*) are transformed by digitonin in 95% EtOH into apparently amorphous digitonides, which separate slowly and are considerably more sol. than those of the usual phytosterols. They are decomposed by hot abs. EtOH, thus leading to the isolation of α- (I), m.p. 114—115°, $[\alpha]_D$ +54·3° in EtOH, and β- (III), m.p. 97°, $[\alpha]_D^{20}$ +49·2° in EtOH, *-tritisterol* and small amounts of an unnamed *substance* (II), m.p. 162—

163°. (I) and (II) usually separate from solvents as gels which are converted into crystals within a few hr. Their behaviour in the Liebermann and Salkowsky reactions differs completely from that of known sterols. (I) gives an *acetate*, m.p. 107—108°, $[\alpha]_D$ +70·4° in $CHCl_3$, and a *dinitrobenzoate*, m.p. 182° [a second *dinitrobenzoate*, m.p. 154—155°, is formed when crude (I) is used]. (II) affords an *acetate*, $[\alpha]_D^{20}$ +55·5° in $CHCl_3$, and a *dibromide*, m.p. 160—162°. (I), (II), and (III) are monohydric alcohols with at least one double linking. They are isomeric or very closely related in composition. They are regarded provisionally as $C_{30}H_{50}O$ and are thus isomeric with amyrin, to which they are very similar in many respects. H. W.

Subsidiary sterols from yeast. IV. Cryptosterol. H. Wieland, H. Pasedach, and A. Ballauf (Annalen, 1937, **529**, 68—83; cf. A., 1931, 1154).—From the residues of the technical prep. of ergosterol the isolation of cryptosterol (I), $C_{30}H_{50}O$, m.p. 138—140°, $[\alpha]_D^{20}$ +58·7° in $CHCl_3$, is best effected by adsorption by Al_2O_3. The composition is confirmed by analysis of the *dibromide* (II), m.p. 180—182° (decomp.), *acetate* (III), m.p. 132—134°, $[\alpha]_D^{20}$ +63·7° in $CHCl_3$, and its *dibromide*, m.p. 165—167°, $[\alpha]_D^{20}$ +32·8° [re-converted into (III) by Zn dust and AcOH in boiling EtOH], *phenylurethane*, m.p. 166—168°, *benzoate*, m.p. 138—140°, $[\alpha]_D^{20}$ +70·5° in $CHCl_3$, and its *dibromide*, m.p. 209—210°, and *dinitrobenzoate*, m.p. 211—212°. The presence of a double linking in (I) is established by the production of (II) and the formation (H_2–PtO_2 in EtOH, Et_2O, or EtOAc) of *dihydrocryptosterol* (IV), $C_{30}H_{52}O$, m.p. 145—146°, $[\alpha]_D^{21}$ +53·9° in $CHCl_3$ {*acetate* (V), m.p. 119—120°, $[\alpha]_D^{20}$ +52·9° in $CHCl_3$; *benzoate* (VI), m.p. 190—191°, $[\alpha]_D^{20}$ +72° in $CHCl_3$}. Further addition of these reactants cannot be effected, but the presence of a second double linking in (I) is established by the coloration given by (IV) and $C(NO_2)_4$ and by the conversion of (IV) by BzO_2H into its *oxide*; analogously (V) and (VI) yield *oxides*, m.p. 143°, $[\alpha]_D^{21}$ +1·7° in $CHCl_3$, and m.p. 193—194°, $[\alpha]_D^{21}$ +21·8° in $CHCl_3$, respectively, which do not give a colour with $C(NO_2)_4$. (I) is therefore a doubly unsaturated alcohol with four isocyclic rings. The *sec.* nature of the OH is established by the oxidation (CrO_3) of (I) to *cryptostadienone*, m.p. 65·5—67°, $[\alpha]_D^{19}$ +76·3° in $CHCl_3$ {*semicarbazone*, m.p. 215—225° (decomp.), transformed by HCl in EtOH into *chlorocryptostenone*, m.p. 134·5—136·5°, $[\alpha]_D^{20}$ +69·1°}. (The nomenclature is based on the term "cryptostane" for the parent hydrocarbon.) Further, (IV) [cryptostenol] is oxidised to *cryptostenone*, $C_{30}H_{50}O$, m.p. 117—118°, $[\alpha]_D^{19}$ +61·3° in $CHCl_3$, the *semicarbazone*, m.p. 220—224°, of which is transformed by NaOEt and N_2H_4,H_2O in EtOH at 200°, into *cryptostene*, $C_{30}H_{52}$, m.p. 74·5—76°, $[\alpha]_D^{19}$ +60·1° in $CHCl_3$. (I) differs from other sterols in composition and colour reaction with H_2SO_4–Ac_2O but resembles them in yielding a *digitonide*. It very closely resembles but is not identical with lanosterol (VII). In constitution it appears to belong to the unexplored group of triterpene alcohols. Epimerisation of (I) or (VII) could not be achieved but epimerism is not the sole cause of the difference between them since the corresponding ketones also differ from one another. H. W.

Sterols, $C_{25}H_{42}O$, m.p. 142—143°, $[\alpha]_D^{32}$ +16·24° in $CHCl_3$, and (?) **$C_{24}H_{44}O$**, m.p. 122°, $[\alpha]_D^{22}$ (?) −83·45° in $CHCl_3$.—See A., III, 190.

Sexual hormones. XXII. Preparation of Δ⁵-3-*epi*hydroxy-17-*trans*hydroxyandrostene and 3-*epi*hydroxy-17-*trans*hydroxyætiocholane. L. Ruzicka, M. W. Goldberg, and W. Bosshard (Helv. Chim. Acta, 1937, **20**, 541—547).—Δ⁵-Androstene-3 : 17-diol 17-monopropionate in AcOH is treated successively with Br and CrO_3 and the product is debrominated by Zn dust in boiling MeOH to (impure) Δ⁵-*testosterone propionate* (I), m.p. (indef.) 135°, $[\alpha]_D$ −17° in EtOH. (I) is hydrogenated (Raney Ni in 95% EtOH) and the product after treatment with digitonin, is hydrolysed to Δ⁵-3-epi*hydroxy*-17-trans*hydroxyandrostene* (II), m.p. 208—209°, $[\alpha]_D$ −54°±2° in EtOH (*diacetate*, m.p. 155—155·5°). Alternatively (II) is obtained by reduction (Raney Ni in 95% EtOH) of Δ⁵-3-*epi*-hydroxyandrosten-17-one. Δ⁵-Androstene-3 : 17-diol 17-monobenzoate is brominated, oxidised, and then debrominated to Δ⁵-*testosterone benzoate*, m.p. (indef.) 170—180°, $[\alpha]_D$ +23° in C_6H_6 (Δ⁴-testosterone benzoate has $[\alpha]_D$ +143° in C_6H_6), which is reduced (Raney Ni in dioxan) to 3-*epi*hydroxy-17-*trans*-hydroxyætiocholane, m.p. 236—236·5°, $[\alpha]_D$ +25° ±1·5° in EtOH (*diacetate*, m.p. 124·5—125·5°), the constitution of which is established by its identity with the product obtained by hydrogenation (Ni or Pt) of 3-*epi*hydroxyætiocholan-17-one. It is identical with the product isolated by Butenandt from male urine. H. W.

Separation of the C_{17}-epimers of œstradiol by digitonin. O. Wintersteiner (J. Amer. Chem. Soc., 1937, **59**, 765).—α-Œstradiol (I), m.p. 178°, $[\alpha]_D$ +81° in 80% EtOH, rapidly forms a *digitonide*, m.p. about 265° (decomp. from 195°) (readily regenerates the diol); β-œstradiol, m.p. 228°, $[\alpha]_D$ +54°, is readily obtained from the mother-liquors. The 3-benzoate of (I) gives a *digitonide* more slowly. Digitonide formation is not an infallible guide to structure. R. S. C.

Iodinating properties of the complex of iodine and silver benzoate. C. Prévost and J. Wiemann (Compt. rend., 1937, **204**, 700—701).—This complex (A., 1935, 738) with CR:CAg gives CR:CI and AgOBz, and with MgRBr gives AgBr and $Mg(OBz)_2$. From PhOH, some $C_6H_2I_3$·OH is formed; H_2O gives AgOI (or 2AgI + $AgIO_3$), and AcOH yields a complex mixture of products. E. W. W.

Synthesis of new local anæsthetics. I. K. N. Gaind (J. Indian Chem. Soc., 1937, **14**, 13—16).—Compounds of type NEt_2·CHR′·CMe(OBz)·CO_2R are prepared, and found to have local anæsthetic action. The cyanohydrin (I) of chloroacetone (II) [improved prep. of (I) from the $NaHSO_3$ derivative of (II)] is hydrolysed to β-chloro-α-hydroxy*iso*butyric acid (III), of which the *CH_2Ph* ester, b.p. 185°/45 mm., is condensed with $NHEt_2$ (in C_6H_6 at 150°), followed by benzoylation of the resulting *base*, to give *benzyl*

β-*diethylamino*-α-*benzoyloxy*isobutyrate, m.p. 63° (*hydrochloride*, m.p. 198°). The *hydrochloride*, m.p. 195°, of the α-p-*nitrobenzoyloxy*-compound is similarly prepared, and is reduced (PtO_2–H_2) to the *hydrochloride*, m.p. 175°, of the α-p-*aminobenzoyloxy*-compound. The Pr^{α}, b.p. 100°/13 mm., and Pr^{β}, b.p. 110°/12 mm., esters of (III) give respectively Pr^{α}, m.p. 56° (*hydrochloride*, m.p. 217°), and Pr^{β} β-*diethylamino*-α-*benzoyloxy*isobutyrate, m.p. 44° (*hydrochloride*, m.p. 207°). From Me α-chloroethyl ketone (IV), β-chloro-α-hydroxy-α-methylbutyric acid is prepared (through the nitrile), and thence the CH_2Ph ester (V), b.p. 180°/20 mm., from which *benzyl* β-*dimethylamino*-α-*benzoyloxy*-α-*methylbutyrate* (VI), m.p. 61° (*hydrochloride*, m.p. 207°), is obtained. If (IV) is not pure, (V) is accompanied by an *isomeride*, b.p. 210°/20 mm., giving an *isomeride*, m.p. 47° (*hydrochloride*, m.p. 235°), of (VI). E. W. W.

Electrochemical oxidation of 2 : 4-dimethylbenzonitrile. F. Fichter and G. Schetty (Helv. Chim. Acta, 1937, **20**, 563—567).—Electrolysis of 2 : 4-$C_6H_3Me_2$·CN in 0·5*N*-H_2SO_4 with a Pb anode and Sn cathode but without diaphragm gives 2 : 4-dimethylbenzylamine (Bz derivative, m.p. 97·5—98°). When a diaphragm is used, the sole product of the oxidation is 6-*cyano*-m-*toluic acid* (I), m.p. 220° (corr.). The yield is >12% with anode c.d. 0·03 amp. per sq. cm.; increase of c.d. causes resinification whereas a purer product is obtained in poorer yield if c.d. is decreased. (I) [Cd (+$6H_2O$) salt; *Me* ester, m.p. 81°] is obtained from 6-amino-*m*-toluic acid and is hydrolysed to 2-methylterephthalic acid. H. W.

Manufacture of (A) *N*-aminoalkylanthranilic acid alkyl esters; (B) *N*-aminoalkylamides of alkylaminobenzoic acids. [Local anæsthetics.] —See B., 1937, 327.

Syntheses with magnesium [derivative of] sodium phenylacetate. V. Aliphatic organomagnesium derivatives. D. Ivanov (Bull. Soc. chim., 1937, [v], **4**, 682—686).—CH_2Ph·CO_2Na reacts with Mg alkyl halides by the same mechanism as CH_2Ph·CO_2MgCl reacts with Mg aryl bromides (A., 1931, 726) to give CH_2Ph·CR(OH)·CHPh·CO_2H in 20—55% yields, and thus from the appropriate MgRX are obtained β-*hydroxy*-αγ-*diphenyl*-β-*ethyl*-, m.p. 135—145° (*Me* ester, m.p. 81—83°) (also synthesised from MgCl·CHPh·CO_2Na and CH_2Ph·COMe), -β-n-*propyl*-, m.p. 152—160°, -β-n-*butyl*-, m.p. 115—120°, and -β-iso*amyl*-, m.p. 166—168°, -*butyric acid*. Hydrolysis of these acids gives good yields of the ketones R·CO·CH_2Ph. Na *p*-chlorophenylacetate behaves similarly, but only very small yields are obtained with the *o*-Cl-compound. CH_2Ph·CO_2MgCl and MgEtBr or $MgPr^{\alpha}Br$ similarly afford a mixture of acids in yields >11%, from which CH_2Ph·COEt (semicarbazone, m.p. 153°; lit. m.p. 133·5°) and CH_2Ph·$COPr^{\alpha}$ are obtained on hydrolysis. J. W. B.

Derivatives of benzoylbenzoic acids. I. 2-(2′- and 2-(4′-hydroxybenzoyl)-3-methylbenzoic acid and 2-(4′-chlorobenzoyl)-3-methylbenzoic acid. II. 2-Benzoyl-3-methylbenzoic acid and 2-benzoyl-6-methylbenzoic acid. III. 3(6?)-Nitro-2-benzoylbenzoic acid, 3(6?)-nitro-2-[2′(4′?)-hydroxybenzoyl]benzoic acid, 3(6?)-nitro-2-(2′ : 5′-dimethylbenzoyl)benzoic acid and 5(4?)-nitro-2-(2′ : 5′-dimethylbenzoyl)benzoic acid. M. Hayashi, S. Tsuruoka, and A. Nakayama (J. Chem. Soc. Japan, 1935, **56**, 1031—1034, 1084—1092, 1093—1101).—I. 3-Methylphthalic anhydride (I) and PhOH afford 2-(2′-, m.p. 220—221°, and 2-(4′-*hydroxybenzoyl*)-, m.p. 197—198°, -3-*methylbenzoic acid*, converted into the isomeric 6-*Me* derivatives, m.p. 141—142° and m.p. 183—184°, by conc. H_2SO_4. (I) and PhCl afford 2-(4′-*chlorobenzoyl*)-3-*methylbenzoic acid*, m.p. 175·5—176°.

II. (I) and C_6H_6 afford 2 : 3-*dibenzoyltoluene*, m.p. 116—117°, and 2-*benzoyl*-6-, m.p. 126—127·5°, and 3-, m.p. 171—172°, -*methylbenzoic acid*, oxidised ($KMnO_4$) to benzophenone-2 : 6-, m.p. 225—226°, and 2 : 3-, m.p. 121—125°, -dicarboxylic acid, respectively; the 3-derivative is converted into the 6-Me isomeride with hot conc. H_2SO_4.

III. The following are prepared by the Friedel–Crafts reaction: 3(6?)-*nitro*-, m.p. 236—237°, and 6(3?)-*nitro*-, m.p. 160—161°, -2-*benzoylbenzoic acids*; 4(5?)-*nitro*-2-(2′ : 5′-*dimethylbenzoyl*)*benzoic acid*, m.p. 191·5—192·5°. Ch. Abs. (*r*)

1 : 2- and 1 : 4-Addition. I. 1 : 4-Addition of potassium *iso*cyanide. A. Michael and N. Weiner (J. Amer. Chem. Soc., 1937, **59**, 744—753).—The following reactions are interpreted in accordance with Michael's general views as proving 1 : 4-addition of KNC (KCN) to αβ-unsaturated ketones, esters, and nitriles, the primary products being K enolates or iminolates, which, if "poorly neutralised," react further with unchanged esters etc. Other views are held to be disproved. Allyl cyanide and KNC in dry MeOH do not react. CHPh:$C(CO_2Me)_2$ and KNC in dry MeOH give a *K* enolate, which with acid gives quantitatively Me_2 β-*cyanobenzylmalonate* (I), m.p. 47·5—48·5°, obtained also in poor yield in aq. MeOH. The K enolate with CH_2PhBr in PhMe gives Me_2 β-*cyano*-α-*benzylbenzylmalonate*, m.p. 117·5—118°, converted into CO_2H·CHPh·CH(CH_2Ph)·CO_2H by HCl at 200°, and with I gives equal amounts of (I) and Me_2 β-*cyanobenzylidenemalonate*, m.p. 74°, hydrogenated to (I) and converted by KNC in dry MeOH into a *K* derivative, which with acid gives *Me* αβ-*dicyano*-β-*phenylpropionate*, m.p. 107—108°, also obtained by I with *Me* αβ-*dicyano*-β-*phenylacrylate*, m.p. 87—88°. Me_2 fumarate and KNC in aq. MeOH give CO_2Me·CH(OMe)·CH_2·CO_2Me (II), CO_2H·CH:CH·CO_2Me, and Me_3 δ-*cyano*-n-*butane*-αβγ-*tricarboxylate* (III), b.p. 178—180°/3 mm. (converted by hydrolysis and dehydration into butane-αβγδ-tetracarboxylic acid and its dianhydride); in cold abs. MeOH (II) and Me_3 2-*cyano*cyclo*pentanone*-3 : 4 : 5-*tricarboxylate* (IV), b.p. 196°/4 mm., are formed; in hot abs. MeOH only (IV) is obtained. The reaction is interpreted as formation by NaOMe of (II) and by KNC of CO_2Me·CH(CN)·CH:C(OMe)·OK and thence of KNC:$C(CO_2Me)$·CH_2·CO_2Me, which with unchanged Me_2 fumarate gives KNC:$C(CO_2Me)$·[CH(CO_2Me)·]$_2$·CH_2·CO_2Me, which yields (III) by saponification and loss of CO_2 and (IV) by a Dieckmann reaction. Hot HCl converts (IV)

into a *substance*, m.p. >300°, which with amyl nitrite gives *cyclo*pentanone-3 : 4-dicarboxylic acid. Me_2 citraconate reacts with KNC after isomerisation to the itaconate; in cold, dry MeOH *Me_2 γ-methoxymethylsuccinate*, b.p. 80·5°/1 mm. (also obtained by NaOMe; corresponding acid, new m.p. 102—103°), and *carbomethoxymethyl-succinimide* or *-imidolactone*, m.p. 80—81°, b.p. 167—175°/1 mm. (gives tricarballylic acid when hydrolysed), are formed; when heated, only the lactone is obtained.

CHPh:CH·COPh and KNC in dry MeOH give *Ph_2 β-cyano-ββ′-tetramethylene diketone* (V), m.p. 237°, converted by CrO_3–AcOH or NaOH–50% EtOH into the substance, $C_{31}H_{23}ON$ (Hann *et al.*, J.C.S., 1904, **85**, 1358); with Br (V) gives HBr and a *substance*, $C_{31}H_{22}ONBr$, m.p. 188—189°, converted by NaOMe into a *substance*, $C_{31}H_{21}ON$, m.p. 188°, which with CrO_3 gives a *substance*, $C_{24}H_{17}ON$, m.p. 235—237° (decomp.). CHPh:CH·CH:C$(CO_2Me)_2$ and KNC in dry MeOH give a *substance*, $C_{29}H_{29}O_8N$, m.p. 143—144°; new interpretations are given of the reactions observed by other workers. Me crotonate gives a complex mixture by secondary reactions.

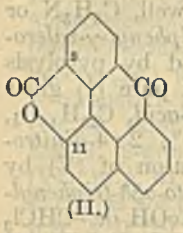
CPh:C·CO_2Me and KNC in dry MeOH give CH_2Bz·CO_2Me and CN·CHPh·CH(CN)·CO_2Me (obtained as main product in aq. MeOH); the intermediates are successively CN·CPh:C:C(OMe)·OK and NK:C:CPh·C(CO_2Me):C:NK. R. S. C.

Preparation of β-4-methoxy-1-naphthoylpropionic acid. K. P. Dave and K. S. Nargund (J. Indian Chem. Soc., 1937, **14**, 58).—This acid (A., 1932, 948) (*Me*, m.p. 56°, and *Et*, b.p. 230°/15 mm., esters) is obtained in much increased yield by using $PhNO_2$ or $(CHCl_2)_2$ as solvent. Its constitution is established by prep. from the 4-bromo-α-naphthyl Me ether Grignard reagent and succinic anhydride. E. W. W.

Substituted succinic acids. II. Conversion of αα′-diarylsuccinamides into diarylacetic acids. J. A. McRae, W. C. Conn, and K. J. Platt (Canad. J. Res., 1937, **15**, B, 46—51).—*p*-C_6H_4Me·CH:CPh·CN with EtOH–KCN–NH_4Cl gives *α-phenyl-α′-p-tolylsuccindinitrile*, m.p. 195°, hydrolysed by 85% H_2SO_4 at 100° to the *diamide* (I), m.p. 294° (corr.) (decomp.), and *α-phenyl-α′-p-tolylsuccinic acid*, m.p. 224° (*Et* ester, m.p. 97°). By similar methods are obtained *α-phenyl-α′-p-chlorophenylsuccin-dinitrile*, m.p. 225°, and *-diamide* (II), m.p. 296° (corr.), and *-succinic acid*, m.p. 240—241°; also *α-phenyl-α′-p-bromophenylsuccin-dinitrile*, m.p. 213—214° (corr.), and *-diamide* (III), m.p. 300—301° (corr.) (decomp.). Like the unsubstituted derivative (A., 1935, 212) (I), (II), and (III) are converted by NaOBr into $CHAr_2·CO_2H$ which are difficult to purify and were isolated and identified as anilides; thus are obtained *phenyl-p-tolyl-*, m.p. 154—155°, *phenyl-p-chlorophenyl-*, m.p. 179° [acid synthesised from *p*-C_6H_4Cl·CH(OH)·CO_2H and C_6H_6 with $SnCl_4$], and *phenyl-p-bromophenyl-*, m.p. 177—178°, *-acetanilide*. J. W. B.

Action of alkaline reagents on diphenylbenzoylbutyrolactone [δ-keto-αβδ-triphenyl-γ-valerolactone]. C. F. H. Allen, E. E. Massey, and R. V. V. Nicholls (J. Amer. Chem. Soc., 1937, **59**, 679—686).—The mixture of Me δ-keto-αβδ-triphenylvalerates, obtained from CH_2Ph·CO_2Me, COPh·CH:CHPh, and NaOMe, with Br–AcOH or –CCl_4 gives isomeric *forms*, (I) m.p. 176°, (II) m.p. 158°, (III) m.p. 147°, and (IV) m.p. 120° [constant-melting mixture of (II) and (III) has m.p. 125°], of *Me γ-bromo-δ-keto-αβδ-triphenylvalerate*. (I) and (II) are unchanged by cold HBr–AcOH, but (III) gives (II), and (IV) gives (I). The naturally obtained mixture with KOAc–AcOH or, less well, C_5H_5N or $NPhMe_2$ gives 65% of *δ-keto-αβδ-triphenyl-γ-valerolactone* (V), m.p. 157°, also obtained by pyrolysis with other substances; pyrolysis of pure (I) gives 80% of MeBr, (V), and a (?) *diketo-acid*, $C_{23}H_{18}O_4$, m.p. 160° (*phenylhydrazone*, m.p. 180°; 2 : 4-*dinitrophenylhydrazone*, m.p. 210°). Reduction of (V) by Zn dust–AcOH or –MeOH gives *δ-keto-αβδ-triphenylvaleric acid*, m.p. 187°, but by HBr–AcOH or –$CHCl_3$ a *form* (VIII) thereof, m.p. 261°. NH_3–EtOH and (V) give slowly *γ-hydroxy-δ-keto-αβδ-triphenylvaleramide*, decomp. 202°, converted by HCl–MeOH into 2-benzoyl-1 : 3-diphenyl*cyclo*propane-1-carboxylamide and regenerated therefrom by H_2SO_4–Ac_2O. $Mg(OMe)_2$–MeOH hydrolyses (V) to *Me γ-hydroxy-δ-keto-αβδ-triphenylvalerate*, *forms*, (VIII) m.p. 180° (*acetate*, m.p. 145°) and (IX) m.p. 145° [converted into (VIII) by cold $Mg(OMe)_2$; *acetate*, m.p. 132°], but simultaneous reduction also occurs. (VIII) and (IX) regenerate (V) at 190°. With NHPh·NH_2 (VII) gives its *phenylhydrazone*, m.p. 224°, but (IX) gives that of (V); the two hydrazones are interconvertible by a little HCl, the former being obtained in hot MeOH, the latter in hot $CHCl_3$. NaOMe converts (V) into 1 : 2 : 4-*triphenyl*-Δ^1-cyclo*pentene*-3 : 5-*dione* (X), m.p. 166° (2 : 4-*dinitrophenylhydrazone*, m.p. 235°), (VII), (CPh·CO)$_2$O, (CHPh·$CO_2H)_2$, m.p. 229°, γ-benzylidene-αβ-diphenyl-γ-crotonolactone (XI), PhCHO, and other products [decomposing when distilled/vac. into BzOH, $(CHPh:)_2$, and COPhMe]. The conversion of (XI) into γ-hydroxy-αβδ-triphenylvalero-γ-lactone (XII) and dehydration thereof are modified. KOH–EtOH converts (X) or (XI) into PhCHO and (CPh·CO)$_2$O; with NaOEt (XI) gives (X) slowly. NH_3–EtOH and (X) at 100° give the lactam of γ-amino-αβδ-triphenyl-$\Delta^{\alpha\gamma}$-butadiene-α-carboxylic acid and γ-keto-αβδ-triphenyl-Δ^{α}-pentene-α-carboxylamide, also obtained similarly from (XI). (X) is stable to KOBr or Br, with dil. HNO_3 gives oils and *p*-NO_2·C_6H_4·CO_2H, with $KMnO_4$ gives PhCHO, BzOH, and CO_2, and with SeO_2 in hot dioxan gives a bimol. *product*, $C_{46}H_{30}O_4$, m.p. 247°, also obtained with PhCHO and BzOH by CrO_3 or O_3 in EtBr; alkaline H_2O_2 gives a *substance*, (?) $C_{23}H_{16}O_3$, m.p. 185°, which yields a (?) dehydrated *diacetate*, $C_{50}H_{34}O_7$, m.p. 155°. $CO(CH_2Ph)_2$, $BzCO_2Et$, and NaOEt (1 mol.) give 27% of (XI) and some (XII); NaOMe as catalyst gives 40% of (II), whereas piperidine or a trace of NaOEt yields *Et α-hydroxy-γ-keto-αβδ-triphenylvalerate*, m.p. 128° (*acetate*, m.p. 101°). The mechanism of the complex changes is discussed. Formation of (X) probably occurs by hydrolysis of (V) to CO_2H·CHPh·CHPh·CH(OH)·COPh, isomerisation thereof to CO_2H·CHPh·CHPh·CO·CHPh·OH, and conversion successively into CO_2H·CHPh·CHPh·CO·CH_2Ph and CO_2H·CPh:CPh·CO·CH_2Ph. R. S. C.

Oxidation products of benzanthrone-8-carboxylic acid. J. L. Grieve and H. G. Rule (J.C.S., 1937, 535—537).—*Me* 8-*bromo*-7-*methoxy*-1-*naphthoate*, m.p. 79° (from the acid through the acid chloride), with *o*-$C_6H_4I{\cdot}CO_2Me$ and Cu-bronze at 175° gives *Me* 7-*methoxy*-8-(*o*-*carbomethoxyphenyl*)-1-*naphthoate* (I), m.p. 137°, hydrolysed by KOH–EtOH to the corresponding *acid*, m.p. 239°. (I) with conc. H_2SO_4 at room temp. gives a theoretical yield of the lactone (II) of 11-hydroxybenzanthrone-8-carboxylic acid, identical with the specimen obtained (A., 1935, 859) by oxidation of benzanthrone-8-carboxylic acid (III) with hot conc. H_2SO_4. The close proximity of the 8 : 11 positions greatly favours the formation of (II) since only with H_2SO_4–AcOH at 80° can a small yield [with much (II)] of the intermediate *Me* 11-*methoxybenzanthrone*-8-*carboxylate*, m.p. 194°, be obtained. This is converted into (II) even by alkaline hydrolysis. Oxidation of (III) with boiling $KMnO_4$–NaOH gives a small yield of *anthraquinone*-1 : 8-*dicarboxylic acid*, m.p. 316—317° (decomp.), decarboxylated (Cu-bronze) to anthraquinone. J. W. B.


(II.)

Bile acids. LI. M. Schenck (Z. physiol. Chem., 1937, **246**, 258—266; cf. this vol., 20).—The acid $C_{24}H_{34}O_{10}N_2$ (Schenck and Kirchhof, A., 1929, 558) with NaOH–$KMnO_4$ at room temp. yields a tetrabasic *acid*, $C_{24}H_{35}O_{10}N$, decomp. 195°, similarly afforded by the ketolactamtricarboxylic acid (I) (A., 1936, 74). Both bilianic acid (II) and the acid $C_{24}H_{33}O_{10}N$, similarly treated, yield cilianic acid. For controlling the oxidation of (I) or (II) by HNO_3, $NH_2{\cdot}SO_3H$ is substituted for $CO(NH_2)_2$ (A., 1936, 1109). The constitution of (I) derivatives is further discussed. F. O. H.

Carbocyclic compounds. XXX. Internal condensation of hexadecane-απ- and octadecane-ασ-dialdehyde. M. Stoll and A. Rouvé (Helv. Chim. Acta, 1937, **20**, 525—541).—Cyclisation of αω-dialdehydes is shown to occur when the length of chain is such that steric hindrance is not experienced and when the solution is so dil. that the mol. has opportunity to become joined at its extremities before encountering a second mol. The $NaHSO_3$ compound of Me θ-aldehydononanecarboxylate in Et_2O is decomposed by Na_2CO_3 and the product is treated with HCl–MeOH and then hydrolysed to the *Me*$_2$ *acetal* of sebacaldehydic acid. Electrolysis of the latter in MeOH affords *octadecane*-ασ-*dialdehyde* *Me*$_4$ *acetal* (I), b.p. 178—185°/0·02—0·03 mm., m.p. 34—35°, from which *octadecane*-ασ-*dialdehyde* (II), m.p. 50—52°, is obtained by means of boiling 10% HCl. (II) cannot be purified from an apparent trace of acid through the semicarbazone or by distillation, which is accompanied by spontaneous polymerisation. *Hexadecane*-απ-*dialdehyde* *Me*$_4$ *acetal* (III) has b.p. 164—165°/0·2 mm., m.p. 21—22°. Condensation of hexadecane-απ-dialdehyde (IV) by $NaNH_2$ in Et_2O containing a little EtOH gives mainly a caoutchouc-like polymeride and non-cryst. products which could not be distilled. Oxidation of the latter with Ag_2O gives a little thapsic acid. Apart from the odour of musk there is no distinct evidence of cyclisation. Under the influence of piperidine acetate (IV) is transformed mainly into resins sol. with difficulty in Et_2O or EtOH; the volatile portions have an odour of musk but appear to give a mixture of semicarbazones. (III) is cyclised by $PhSO_3H$ in boiling C_6H_6 to Δ^1-cyclo*pentadecene*-1-*aldehyde*, $CH_2<^{CH\longrightarrow}_{[CH_2]_{12}}>C{\cdot}CHO$, [*semicarbazone*, m.p. 147—149° (152°)], hydrogenated (Ni in EtOH) to cyclo*pentadecylcarbinol* (V), b.p. 133—136°/0·08 mm. [3 : 5-*dinitrobenzoate* (VI), m.p. 100—101°]. Exaltone, $CH_2Cl{\cdot}CO_2Et$, and $NaNH_2$ in Et_2O slowly yield *Et* cyclo*pentadecylglycidate*, hydrolysed to cyclo*pentadecylglycidic acid* [(?) corresponding *amide*, m.p. 173—175°], which passes when distilled into cyclo*pentadecaldehyde*, b.p. 108—112°/0·05 mm.; the latter substance is reduced to (V) which is identified as (VI). Attempts to cyclise (II) in alkaline media were unsuccessful but (I) is converted by $PhSO_3H$ in boiling C_6H_6 into Δ^1-cyclo*heptadecene*-1-*aldehyde*, b.p. 130—133°/0·05 mm. [*semicarbazone*, m.p. 143—143·5° (corr.)], which is hydrogenated to cyclo*heptadecylcarbinol* (VII), b.p. 160—163°/0·12 mm. [*H phthalate*; 3 : 5-*dinitrobenzoate* (VIII), m.p. 90·5—91°]. (VII) is readily transformed into the corresponding *stearate*, b.p. 260—270°/0·2 mm., m.p. about 25°, which could not be dehydrated. Esterification of (VII) with HBr and passage of the bromide over $BaCl_2$ yields an unsaturated *hydrocarbon*, ozonisation of which in EtOAc at −50° followed by catalytic decomp. of the ozonide appears to give a CO-aldehyde (*disemicarbazone*, $C_{20}H_{40}O_2N_6$, m.p. 163—165° to a cloudy liquid which becomes transparent at 167°). Direct dehydrogenation of (VII) by $AlCl_3$ at 310—320°/0·1 mm. affords *methylene*cyclo*heptadecane*, b.p. 112—115°/0·05 mm., ozonised to a substance with a very feeble odour of musk (*semicarbazone*, m.p. 136—140°). Dihydrocivetone, $CH_2Cl{\cdot}CO_2Et$, and $NaNH_2$ in Et_2O afford *Et* cyclo*heptadecylglycidate*, b.p. 143—150°/0·05 mm., hydrolysed to cyclo*heptadecylglycidic acid*, which decomposes when distilled in a vac. to cyclo*heptadecaldehyde*, b.p. 123—125°/0·05 mm. (*semicarbazone*, m.p. 132—135°), which is reduced to (VII), identified as (VIII). H. W.

Ethylenic aldehydes. M. Meyer (Compt. rend., 1937, **204**, 508—509).—α-Ethoxy-β-styrylpropionic acid and α-ethoxy-η-vinylundecoic acid (cf. this vol., 47) at 280—300° afford (cf. A., 1933, 491) *cinnamylformaldehyde* (δ-*phenyl*-Δ$^\gamma$-*butenaldehyde*), b.p. 130—132°/14 mm. [*semicarbazone*, m.p. 212—214° (block)], and Δ$^\lambda$-*dodecenaldehyde*, b.p. 100—102°/3·5 mm. (*semicarbazone*, m.p. 91°), respectively. J. L. D.

αβ-Diphenylpropaldehyde. H. Burton and C. W. Shoppee (J.C.S., 1937, 546—549).—$CH_2Ph{\cdot}CHPh{\cdot}COCl$ and NH_2Ph afford αβ-diphenylpropanilide, m.p. 166°, converted by PCl_5 in $C_2H_2Cl_4$ at 140° into the iminochloride, reduced ($SnCl_2$, Et_2O–HCl–$C_2H_2Cl_4$) to αβ-*diphenylpropaldehyde* (I), b.p. 170°/11 mm., m.p. 54° (*semicarbazone*, m.p. 124—125°; 2 : 4-*dinitrophenylhydrazone*, two *forms*, m.p. 148—152°, and m.p. 199°). The compound, m.p. 116°, described as the hydrate of (I) by Stoermer *et al.* (A., 1926, 160) is actually $CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}OH$ (Kohler *et al.*, A., 1934, 523: Jarrousse, A., 1936,

1252) [*semicarbazone*, m.p. 191—192° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 164—164·5°], oxidised by Nessler's reagent in dioxan at 15° to $CH_2Ph{\cdot}CO{\cdot}COPh$, but with Nessler's reagent in $COMe_2$ it affords *δε-diketo-γε-diphenyl-β-methyl-Δ$^{\beta}$-pentene*, m.p. 123°, which with O_3 gives $COMe_2$, BzOH, and $BzCO_2H$ [characterised as 3-*keto*-2-*phenyl*-3 : 4-*dihydroquinoxaline*, m.p. 247°, which is formed with *o*-$C_6H_4(NH_2)_2$]. (I) could not be obtained by catalytic reduction (Adams) of $CHPh{:}CPh{\cdot}CHO$, but is oxidised by Ag_2O to $CH_2Ph{\cdot}CHPh{\cdot}CO_2H$. (I) with $CH_2(CO_2H)_2$ in C_5H_5N–piperidine affords *γδ-diphenyl-Δ$^{\alpha}$-pentenoic acid*, m.p. 89°. J. W. B.

Coordinate valency rings. III. Inner complex salts of iron and manganese. T. Tsumaki (J. Chem. Soc. Japan, 1935, **56**, 1329—1331; cf. A., 1935, 750).—The Fe derivative of trisalicylaldehyde-di-imine (I), $C_{21}H_{15}O_3N_2Fe$, was prepared by the interaction of hot solutions of (*a*) 4 g. of salicylaldehyde, 10 g. of 25% aq. NH_3, and 150 c.c. of EtOH and (*b*) 80 c.c. of 5·0% Fe NH_4 alum. Mn derivatives of (I) and of salicylaldehydebenzylimine (II) and the hydroxy-Mn derivative of (II) were prepared similarly. Ch. Abs. (*c*)

Hydroxymethylene compounds. R. Keller (Helv. Chim. Acta, 1937, **20**, 436—450).—Hydroxymethylenephenylacetaldehyde (I) (20% excess) and NH_2Ph afford anilinomethylenephenylacetaldehyde (II), m.p. 137°. With 2 mols. of NH_2Ph (I) yields the anil, $NHPh{\cdot}CH{:}CPh{\cdot}CH{:}NPh$, m.p. 130°, hydrolysed by 10% HCl to (II). (I) and anthranilic acid yield o′-*carboxyanilinomethylenephenylethylideneanthranilic acid*, m.p. 251°, hydrolysed to o′-*carboxyanilinomethylenephenylacetaldehyde*, m.p. 220°, obtainable with difficulty by condensation of the components. According to conditions *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$ yields p′-*carbethoxyanilinomethylenephenylacetaldehyde*, m.p. 131°, or the Schiff's *base*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}CPh{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO_2Et$, m.p. 145°. (I) and α-$C_{10}H_7{\cdot}NH_2$ (1 : 1) give 1-*naphthylaminomethylenephenylacetaldehyde* (III), m.p. 82°, or (1 : 2) β-*phenyl*-β-*naphthylaminomethylene-ethylidene-α-naphthylamine* (IV), m.p. 233°. The conversion of (III) into a semicarbazone or of (III) into (IV) could not be effected. Benzoyloxymethylenephenylacetaldehyde and α-$C_{10}H_7{\cdot}NH_2$ (1 : 2) afford (IV) and BzOH. β-*Naphthylaminomethylenephenylacetaldehyde*, m.p. 282° (from the reactants in any ratio), does not react with $NHPh{\cdot}CO{\cdot}NH{\cdot}NH_2$, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl, or NH_2Ph and is stable towards boiling HCl. p-*Toluidinomethylenephenylacetaldehyde* has m.p. 152°. *o*-$C_6H_4Me{\cdot}NH_2$ and (I) yield β-*phenyl*-β-o′-*toluidinomethylene-ethylidene*-o-*toluidine*, m.p. 129°. α-Aminocamphor and (I) give the Schiff's base, $\begin{matrix}CO\\ C_8H_{14}\end{matrix}\!\!>\!CH{\cdot}NH{\cdot}CH{:}CPh{\cdot}CH{:}N{\cdot}CH\!<\!\!\begin{matrix}CO\\ C_8H_{14}\end{matrix}$, m.p. 156° (*perchlorate*; *hydrochloride*; *sulphate*), which exhibits complete abnormal rotation dispersion. *Phenylcarbazidomethylenephenylacetaldehydephenylsemicarbazone*, m.p. 216°, is obtained from (I) and $NHPh{\cdot}CO{\cdot}NH{\cdot}NH_2$ in all proportions. (I) and $NHPh{\cdot}OH$ in HCO_2H or AcOH afford diphenyl*iso*-oxazolone, $\begin{matrix}CPh{\cdot}CO\\ CH{\cdot}NPh\end{matrix}\!\!>\!O$, m.p. 167°, hydrolysed by KOH–H_2O–EtOH to *trans*-phenylhydroxylaminomethylenephenylacetic acid, m.p. 132°. Under somewhat different conditions the product obtained is *acetoxymethylenephenylacetanilide*, m.p. 141—142° hydrolysed to $CH_2Ph{\cdot}CO{\cdot}NHPh$, m.p. 118°, or N-*phenylisophenylacetaldoxime*, m.p. 146°. Hydroxymethylenephenylacetonitrile in EtOH is hydrogenated (Ni on clay) under pressure to β-phenylpropylamine, b.p. 90°/13 mm. (*hydrochloride*; *H oxalate*, m.p. 137°; *Bz* derivative, m.p. 94°), and (?) *di*-β-*phenylpropylamine*, b.p. 180°/13 mm. (*H oxalate*, m.p. 216°). Condensation of (I) with KCN and anhyd. HCN yields *α-hydroxy*-β-*phenylsuccinonitrile* (V), m.p. 89°, which in presence of traces of moisture passes into the corresponding *nitrile-amide* (II), m.p. 62°. (V) is transformed by conc. HCl at 100° into *α-hydroxy*-β-*phenylsuccinimide*, m.p. 177°, which is more sol. in aq. NaOH than in H_2O. Boiling 30% NaOH slowly transforms (V) or (VI) into NH_3 with some HCN and $CH_2Ph{\cdot}CO_2H$. H. W.

Polymembered ring systems. VI. Tendency of formation of polymethylene ketones with more than twenty carbon atoms. K. Ziegler and W. Hechelhammer (Annalen, 1937, **528**, 114—142; cf. A., 1934, 1220).—Nitriles with 20—27, 29, 30, and 34 C are obtained partly from the corresponding dibromides and partly from the dicarboxylic acids and their purity is placed beyond doubt by the regularities of the m.p. in the odd and even series. These are converted into the corresponding cyclic ketones by the process described previously (*loc. cit.*). Reasons are advanced for basing the comparative tendency of ring formation on the yield of crude ketone and, on this basis, there is a feeble periodicity in the region C_{20}—C_{30}. The form of the m.p. graph of cyclic ketones beyond C_{25} cannot yet be definitely ascertained but uniformity in physical properties, such as would be expected from homologous substances of this mol. magnitude, is not observed. In the relationship between mol. depression of the f.p. and no. of ring members the position of *cyclo*dodecanone is exceptional. Thence the mol. depression increases but the difference between neighbouring homologues is small. The subsequent decline is irregular and "odd" and "even" graphs are obtained pointing to a pronounced change in the fine structure of the mols. at about C_{23}.

H esters of dicarboxylic acids with $\not>12$ C are conveniently obtained by heating the acid with MeOH and 2-$C_{10}H_7{\cdot}SO_3H$ until the titre does not diminish further or by heating the acid and normal ester with MeOH–H_2O containing 2-$C_{10}H_7{\cdot}SO_3H$. The method is not readily applicable to more complex H esters, which are best obtained by repeated partial hydrolysis of the normal esters. Electrolysis is carried out by Ruzicka's method but with use of a Pt gauze anode. The cyclisation of απ-dicyanohexadecane to *α-cyano*cyclo*heptadecanone*, b.p. 139—141°/0·001 mm., m.p. 43°, and its oxidation to *pentadecane-αω-dicarboxylic acid*, m.p. 118° (*Et*$_2$ ester, m.p. 43°), are described. For the Bouveault–Blanc reduction of esters to glycols the use of synthetic

(not fermentation) BuOH is recommended. This is dehydrated by addition of somewhat > the amount of Na required by the H_2O present, followed by the corresponding quantity of BuOAc, after which the mixture is heated until hydrolysis is complete; after cooling the pptd. NaOAc is removed. The ester in this solvent is added to the Na with brisk stirring at about 70° and the temp. is gradually raised to 140—150°. The glycols are converted into the dibromides by HBr–AcOH at about 100° (1 : 25-*dibromopentacosane*, m.p. 63°, b.p. 208°/high vac.) and thence into the nitriles by pure KCN in 90% EtOH (1 : 25-dicyanopentacosane, m.p. 75·5—76·5°; *αψ-dicyanotricosane*, m.p. 69°). Interaction of the higher bromides with NaOEt (4 mols.) and $CH_2(CO_2Et)_2$ (8 mols.) (*Et*$_4$ *tricosane-αααω-tetracarboxylate*, m.p. 49°; *Et*$_4$ *heptacosane*-1 : 1 : 27 : 27-*tetracarboxylate*, m.p. 52°), hydrolysis of the esters, conversion of the acids into nitriles, and cyclisation of the latter are described. The following data appear new: cyclo*heneicosanone*, b.p. 156°/0·2 mm., m.p. 49—50° (*semicarbazone*, m.p. 49—50°); cyclo*docosanone*, b.p. 158—160°/0·25 mm., m.p. 41—42° (*semicarbazone*, m.p. 176—177°); cyclo*tricosanone*, b.p. 158—161°/0·2 mm., m.p. 39—40° (*semicarbazone*, m.p. 175—176°); cyclo*tetracosanone*, b.p. 186—189°/0·3 mm., m.p. 36—38° (*semicarbazone*, m.p. 170·5—171·5°); cyclo*pentacosanone*, b.p. 198—199°/0·2 mm., m.p. 37·5—38·5° (*semicarbazone*, m.p. 170—171°); cyclo*hexacosanone*, b.p. 195—198°/0·3 mm., m.p. 41·5—43° (*semicarbazone*, m.p. 165—166°); cyclo*octacosanone*, b.p. 217—219°/0·3 mm., m.p. 49—50° (*semicarbazone*, m.p. 161°); cyclo*nonacosanone*, b.p. 225—227°/0·3 mm., m.p. 45—46° (*semicarbazone*, m.p. 45—46°); cyclo*tritriacontanone*, b.p. 235—240°/0·2 mm., m.p. 52·5—53·5° (*semicarbazone*, m.p. 151·5—152·5°). H. W.

γ-Benzoylbutyronitrile [**δ-keto-δ-phenyl-γ-valeronitrile**]. C. F. H. Allen and W. L. Ball (J. Amer. Chem. Soc., 1937, **59**, 686—689).—Bz·$[CH_2]_3$·CO_2Me and NH_3 in aq. EtOH give an unstable *compound*, Bz·$[CH_2]_3$·$CO·NH_2,NH_3$, m.p. 120—121°, which decolorises Br and $KMnO_4$ and in CCl_4, $CHCl_3$, C_6H_6, or hot H_2O gives *δ-keto-δ-phenylvaleramide* (I), m.p. 144° [2 : 4-*dinitrophenylhydrazone* (II), m.p. 195—196°], very readily hydrolysed; long reaction gives a poor yield of (I) and a *substance*, m.p. 320°, possibly $\left(\begin{matrix}NH\cdot CO\cdot CH_2\\ C(CH_2Ph):CH\end{matrix}>C\right)_2$. Hot Ac_2O converts pure (I) into the *nitrile* (III), b.p. 135—140°, m.p. 38° (*dinitrophenylhydrazone*, m.p. 173—175°; *semicarbazone*, m.p. 176—177°), which is readily hydrolysed by acid, but with HBr–$CHCl_3$ gives (?) the "imide bromide," m.p. 205—210°, and with dry KOAc–EtOAc affords (I). When heated alone or in AcCl, (I) gives 2-keto-6-phenyl-1 : 2 : 3 : 4-tetrahydropyridine, which is also obtained by passing dry NH_3 into (I) at 160—170° and with 2 : 4-$(NO_2)_2C_6H_3$·$NH·NH_2$ yields (II). (I) may be a mixture of the open-chain form with $CH_2<\begin{matrix}CO—NH\\ CH_2\cdot CH_2\end{matrix}>CPh\cdot OH$. Br converts (III) into a complex mixture, containing a little 6-phenyl-2-pyridone, probably formed by partial cyclisation of (III) by HBr prior to reaction with Br. 6-Amino-2-phenylpyridine could not be obtained.

Cl·$[CH_2]_3$·COPh with KCN or CuCN gives excellent yields of benzoyl*cyclo*propane. R. S. C.

Action of mixed organo-magnesium compounds on phenylhydrazones of ketones. New reaction of organo-magnesium compounds. P. Grammaticakis (Compt. rend., 1937, **204**, 502—504; cf. A., 1936, 837).—The phenylhydrazones of $COPh_2$, COPhMe, and $COMe_2$ with MgEtBr afford, respectively, CPh_2:NPh, α-phenyl- and α-methyl-indole. In each case some of the original ketone, NH_3, and NH_2Ph are formed. Cyclisation is the principal reaction when the structure of the original ketone permits it. J. L. D.

Formation of nitrones by action of aromatic nitroso-compounds on methylene ketones. A. Schönberg and R. Michaelis (J.C.S., 1937, 627—628).—3 : 3-Diphenyl-1-hydrindone and PhNO or *p*-NMe_2·C_6H_4·NO in warm aq. EtOH–NaOH give, respectively, 3 : 3-*diphenylindanedione-2-anil oxide*, m.p. 204°, and -2-*p-dimethylaminoanil oxide*, m.p. 233—234°, both hydrolysed by boiling 45% H_2SO_4 to 3 : 3-*diphenylindanedione*, m.p. 152—153°. The mechanism suggested also explains the formation of the dinitrone from diazomethane and PhNO thus: CH_2N_2 + PhNO → N_2 + CH_2:NPhO → $[CH\cdot NPh\cdot OH]_2$ + PhNO → $[CH:NPhO]_2$ + NHPh·OH. J. W. B.

Pyrene. I. K. Dziewoński and L. Sternbach (Rocz. Chem., 1937, **17**, 101—104).—Pyrene and AcCl in $PhNO_2$ in presence of $AlCl_3$ at 20° yield *methyl* 3-*pyrenyl ketone*, (I), m.p. 94° [*oxime* (II), m.p. 198°; *phenylhydrazone*, m.p. 168°; *picrate*, m.p. 160°]. (II) yields 3-*acetamidopyrene*, m.p. 260°, by the Beckmann change, whence 3-aminopyrene, m.p. 117°. (I) and S (2 hr. at 230—260°) give *bis*-4 : 3-*pyrenothiophenindigo*, m.p. >400°. (I) and MeMgI in Et_2O afford 3-iso*propenylpyrene*, m.p. 61·5—62·5° (*picrate*, m.p. 146—147·6°). R. T.

Ketimine compounds formed in the microdetection of magnesium and beryllium.—See A., I, 319.

Relations between chemical properties and "colour" of methoxybenzophenoneoximes and their derivatives. M. Martynoff (Ann. Chim., 1937, [xi], **7**, 424—492).—The action of CH_2PhCl and NaOEt on methoxybenzophenoneoximes gives a mixture of *O*-compounds (I) the constitution of which is established by their synthesis with NH_2·O·CH_2Ph, and *N*-derivatives (II), the structure of which is based on their hydrolyses by HCl, their reduction by Na and abs. EtOH, and their spectroscopic behaviour, which establish the formula OMe·C_6H_4·CHPh·NO:CHPh. In some cases (II) are hydrolysed by HCl to NH_2OH owing to previous isomerisation to OMe·C_6H_4·CHPh·O·N:CHPh. (I), like the oximes from which they are derived, are reduced by Na and EtOH to primary amines, fission occurring between O and N. (II) under like conditions afford *sec.* amines with similar form and length of chain. Photochemical stereomutation of (I) resembles that of the parent oximes whereas (II) are rapidly decomposed and resinified by ultra-violet

light. Replacement of H of the functional group of oximes by CH_2Ph causes slight increase in the coeff. of absorption and slight displacement of the bands towards the visible end. The entirely different character of the absorption of (II) proves a profound change of structure. The *syn-* and *anti*-forms of (I) differ from one another somewhat in colour but the differences are small and consist essentially in a displacement of the bands and a variation in the intensity of the absorption without sensible modification in the form of the bands. The methoxybenzophenones are most conveniently obtained by interaction of the requisite methoxybenzoyl chloride with ZnPhBr (obtained from MgPhBr and $ZnCl_2$ in Et_2O) in PhMe. The prep. of the oximes from the ketones or ketimines is described. The following observations appear new. Labile *o*-methoxybenzophenoneoxime, m.p. 159° in a preheated bath, can be obtained only in cold solution. o-*Methoxybenzophenoneketimine*, m.p. 45°, is obtained from *o*-OMe·C_6H_4·CN and MgPhBr or from PhCN and *o*-OMe·C_6H_4·MgBr. m-*Methoxybenzophenoneoxime* has m.p. 98°; a labile form could not be isolated. The product, m.p. 116°, appears to be the more stable form of *p*-methoxybenzophenoneoxime; the relative ease of isolation and of interconversion of the two forms indicates a smaller influence of OMe in the *p*- than in the *o*- or *m*-position on the orientation of OH. o-*Methoxybenzophenoneoxime CH_2Ph ether*, m.p. 78°; N-o-*methoxybenzhydrylbenzaldoxime* (VI), m.p. 158·5—159·5°, hydrolysed by HCl to PhCHO, *di*-o-*methoxybenzhydryl ether*, m.p. 136—137° (obtained also by the action of heat on *o*-methoxybenzhydrol), NH_2OH, and O-o-*methoxybenzhydrylbenzaldoxime*, m.p. 85° (reduced by Na and EtOH to $CH_2Ph·NH_2$, identified as NHPh·CO·NH·CH_2Ph); reduction of (III) by Na and EtOH affords *benzyl*-o-*methoxybenzhydrylamine* (*hydrochloride*, m.p. about 150—155°; *Ac* derivative, m.p. 121°). m-*Methoxybenzophenoneoxime CH_2Ph ether*, b.p. 214—216°/>0·5 mm.; N-m-*methoxybenzhydrylbenzaldoxime*, m.p. 113—115°, converted by HCl into PhCHO, NH_2OH, and non-cryst. material not volatile without decomp.; p-*methoxybenzophenoneoxime CH_2Ph ether*, m.p. 74°; N-p-*methoxybenzhydrylbenzaldoxime*, m.p. 168°, converted by HCl into PhCHO and material which, when distilled, gives αβ-*diphenyl*-αβ-*di*-p-*anisylethane*, m.p. 189°. H. W.

Monoximes of aromatic-aliphatic α-diketones. New α-diketones and their dioximes. C. Philipp and S. Müller (Annalen, 1937, **528**, 296—302).—Oximation of diketones, COAr·COAlk, in an alkaline or acid medium gives first the β-monoxime (I), COAr·CAlk:N·OH, and further reaction occurs only when this stage has been completed. In acid solution the product invariably contains considerable amounts of (I) as well as dioxime (II). Further oximation of the α-monoxime (III), OH·N:CAr·CO·Alk, gives (II) exclusively. Treatment of (II) with dil. H_2SO_4 affects the α-:N·OH first. The conversion of monoxime into diketone by boiling dil. H_2SO_4 proceeds smoothly with (I) though frequently more slowly than with (III). Hydrolysis of (III) is accompanied by partial isomerisation to (I). The following compounds appear new: *acetyl*-p-*toluoyl*-β-*monoxime*, m.p. 116°, and -*dioxime*, m.p. 226°; *acetyl*-p-*chlorobenzoyl*, m.p. 32° (slowly decomp. with formation of *p*-$C_6H_4Cl·CO_2H$ by hot acids), its β-*monoxime*, m.p. 113°, and *dioxime*, m.p. 220°; *acetyl*-p-*ethoxybenzoyl*, b.p. 178°/35 mm. (β-*monoxime*, m.p. 119°; *dioxime*, m.p. 209°). Contrary to Borsche (A., 1907, i, 326), the product of the hydrolysis of acetyl-*p*-anisoyl-α-monoxime is the β-monoxime, not pyruv-*p*-anisidide. H. W.

Transformation of αγ-amino-ketones into αδ-nitro-ketones. B. Reichert and H. Posemann (Arch. Pharm., 1937, **275**, 67—83).—$MeNO_2$ condenses in presence of alkali at the β-C with 1, 2, or 3 mols. of αβ-unsaturated ketones according to the nature of the ketone. Isolation of vinyl ketones from bases, COR·$[CH_2]_2$·NMe_2, is usually impossible owing to decomp., but when the bases are heated with $MeNO_2$ and alkali condensation of the "nascent" vinyl ketone gives good yields of the γ-nitro-ketones. Benzylidene-ketones condense in this way, but dibenzylidene-ketones condense with only one mol. of $MeNO_2$. The nitro-ketones do not condense with aldehydes, but with isatin, best in presence of NH_3, give 2-substituted 3-β-nitroethylquinoline-4-carboxylamides. COPh·$[CH_2]_2$·NMe_2, $MeNO_2$, and KOH in hot MeOH give γ-nitrobutyrophenone (I), m.p. 66° [*semicarbazone*, m.p. 163° (decomp.), hydrolysed by $H_2C_2O_4$ without decomp.], δ-*nitro*-αη-*diphenylheptane*-αη-*dione* (II), m.p. 133°, and δ-*nitro*-αη-*diphenyl*-δ-γ'-*keto*-γ'-*phenylpropylheptane*-αη-*dione*, m.p. 152°; under Kohler's conditions (A., 1923, i, 1118) much (I) and some (II) are formed. Allen and Bell's compound, m.p. 132° (A., 1934, 1103), was a mixture. The structure of (I) is proved by reduction, best by Clemmensen's method, to 2-phenylpyrrolidine. (I) and isatin in aq. MeOH–NH_3 give 2-*phenyl*-3-β-*nitroethylquinoline*-4-*carboxylamide*, m.p. 243—244° (decomp.), which cannot be hydrolysed without decomp. *p*-OMe·C_6H_4·CO·C_2H_4·NMe_2, $MeNO_2$, and NaOMe give 4-*methoxy*-γ-*nitrobutyrophenone*, m.p. 69—70° [*semicarbazone*, m.p. 177—178° (decomp.)], and thence 2-p-*anisyl*-3-β-*nitroethylquinoline*-4-*carboxylamide*, m.p. 217° (cannot be hydrolysed). Similar reactions lead to 3 : 4-*dimethoxy*-γ-*nitrobutyrophenone*, m.p. 95—96° [*semicarbazone*, m.p. 182—183° (decomp.)], δ-*nitro*-αη-*di*-(3 : 4-*dimethoxyphenyl*)*heptane*-αη-*dione*, m.p. 125—126°, 2-β-*nitroethyl*cyclo*hexanone*, b.p. 160°/14 mm. [*semicarbazone*, m.p. 151—152° (decomp.)], and ε-*nitropentan*-β-*one* (from COMe·CH:CH_2), b.p. 115°/12 mm. [*semicarbazone*, m.p. 141° (decomp.)]. The appropriately substituted COMe·CH:CHPh give ε-*nitro*-p-*anisyl*- (III), m.p. 85—86° [*semicarbazone*, m.p. 176° (decomp.)], -3 : 4-*dimethoxyphenyl*-, m.p. 90—91° [*semicarbazone*, m.p. 171—172° (decomp.)], and -3 : 4-*methylenedioxyphenyl*-*pentan*-β-*one*, m.p. 97—98° [*semicarbazone*, m.p. 175—176° (decomp.)], and thence by H_2–Pd or Zn–Hg–HCl 4-3' : 4'-*dimethoxyphenyl*- [*hydrochloride*, m.p. 211—212° (decomp.)], and 4-p-*anisyl*-2-*methylpyrrolidine* (*picrate*, m.p. 157—158°). CHPh:CH·CO·$C_6H_2(OMe)_2$·NO_2 gives δ-*nitro*-β-*phenyl*-α-2-*nitro*-4 : 5-*dimethoxyphenylbutan*-α-*one*, m.p. 135—136°, which with Pd–C in AcOH–EtOAc absorbs $3H_2$ to give δ-*nitro*-β-*phenyl*-α-2-*amino*-3 : 5-*dimethoxy*-

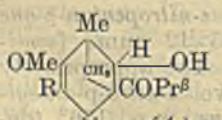
phenylbutan-α-one, m.p. 156—157° (*Ac* derivative, m.p. 158°, hydrolysed by alkali without decomp.; couples with β-$C_{10}H_7$·OH after diazotisation). $CO(CH{:}CHPh)_2$ gives *ζ-nitro-αε-diphenyl-Δ^a-hexen-γ-one*, m.p. 118—120°, which gives a *semicarbazone*, m.p. 203°, but is probably enolic since it gives a red $FeCl_3$ colour and immediately decolorises Br and $KMnO_4$. $CO(CH{:}CH{\cdot}C_6H_4{\cdot}OMe)_2$ gives the *keto-*, m.p. 140° (reacts slowly with Br and $KMnO_4$; no $FeCl_3$ colour), and *enol-form*, m.p. 120—122° (reacts at once with Br and $KMnO_4$; red $FeCl_3$ colour), of *ζ-nitro-αε-p-anisyl-Δ^a-hexen-γ-one*, the keto-form being also obtained from (III) and *p*-OMe·C_6H_4·CHO. R. S. C.

Condensation of naphthalyl chloride with acetoacetic ester. J. Suszko and B. Szych (Rocz. Chem., 1937, **17**, 111—117).—Naphthalyl chloride and Et sodioacetoacetate in C_6H_6 at 0° yield Et *peri*naphthindandionecarboxylate, from which a mixture of the free acid and *peri*naphthindandione is obtained by heating in alkaline solution. R. T.

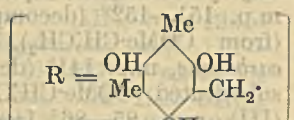
Mixed phenoxyphenyl, diphenylyl, and furyl alkyl ketones.—See B., 1937, 328.

Reduction of 2-acylresorcinols. I. Reduction of 2-acetylresorcinol and its dimethyl ether. D. B. Limaye and (Miss) I. Ghate (Rasāyanam, 1936, **1**, 39—42).—2-Acetylresorcinol Me_2 ether (I) is reduced by Na–EtOH to 2 : 6-*dimethoxyphenylmethylcarbinol*, m.p. 58°, and to 2-*ethylresorcinol* Me_2 *ether* (II), m.p. 60°, demethylated ($AlCl_3$) to 2-ethylresorcinol (III). (III) is also obtained from 2-acetylresorcinol by Clemmensen reduction, which in other experiments gave resorcinol. Clemmensen reduction of (I) in some experiments gave (II), and in others resorcinol Me_2 ether, also obtained by boiling (I) with HCl. 2-*Propionylresorcinol*, m.p. 139°, yields 2-*propylresorcinol*, m.p. 100—102°. E. W. W.

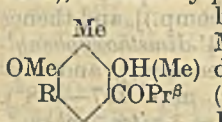
Anthelmintics: kousso. I. Protokosin. B. A. Hems and A. R. Todd (J.C.S., 1937, 562—566).—Protokosin (I), $C_{22}H_{28}O_7$, m.p. 182°, $[\alpha]_D$ +8·0° in $CHCl_3$ (amorphous Ac_3 derivative, m.p. 90—100°: contains 1 OMe, 3 OH, 4 *C*-Me), is isolated in 0·4% yield from the Et_2O extract of dried kousso (*Hagenia abyssinica*) together with kosotoxin (cf. Leichsenring, A., 1894, i, 424), but no trace of kosidin (Lobeck, A., 1902, i, 167) [probably impure (I)] could be detected. When boiled with Zn dust–20% aq.



(*A.*)



NaOH (I) affords $Pr^\beta CO_2H$ (equiv. to 1 $Pr^\beta CO$ per mol.), *C*-trimethylphloroglucinol, and kosin, separated by fractional crystallisation from MeOH into α- (II), m.p. 158° (Ac_3 derivative, m.p. 123°), and β-kosin (III), m.p. 120° (Ac_3 derivative, m.p. 155°), both of which are isomeric with (I) but contain 2 OMe. Fusion of (I) with KOH at 300° gives *C*-monomethylphloroglucinol, identical with a specimen synthesised by the method of Curd *et al.* (A., 1933, 609). Other degradation experiments failed to give definite products, but the structure (*A*) is tentatively suggested for (I), (II) and (III) then being represented by the isomeric forms of (*B*). J. W. B.



(*B.*)

Dehydrogenation of secondary alcohols to ketones. I. Preparation of sterol-ketones and sexual hormones. R. V. Oppenauer (Rec. trav. chim., 1937, **56**, 137—144).—The method consists in the reversal of the method of Meerwein (A., 1925, i, 1239) and Ponndorf (A., 1926, 520) for the reduction of ketones with Al alkoxides. The sterol is refluxed with a considerable excess of $COMe_2$, C_6H_6, and $Al(OBu^\gamma)_3$, moisture being excluded. In this way cholestenone (I) is obtained from cholesterol (II), *ergostatrienone*, m.p. 131—132·5°, $[\alpha]_D$ −15·7° in $CHCl_3$ [*semicarbazone*, m.p. 252—254° (decomp.); *Me ether*, m.p. 140—141°, of the *enol*], from ergosterol, androstenedione from dehydroandrosterone, progesterone from pregnenolone, methyltestosterone from 17-methyl-Δ$^{5:6}$-androstene-3 : 17-diol, and testosterone acetate from 17-acetyl-Δ$^{5:6}$-androstene-3 : 17-diol. Curves are given showing the rate and extent of conversion of (II) into (I) for various initial amounts of (II), $COMe_2$, and $Al(OBu^\gamma)_3$. H. G. M.

Sterols. VIII. Preparation of androstanedione from *allo*pregnanediol. R. E. Marker, O. Kamm, D. M. Jones, and T. S. Oakwood. **IX. Isolation of *epi*pregan-3-ol-20-one from human pregnancy urine.** R. E. Marker, O. Kamm, and R. V. McGrew. **X. Cholesterol derivatives.** R. E. Marker, O. Kamm, G. H. Fleming, A. H. Popkin, and E. L. Wittle. **XII. Synthetic preparation of *epiallo*pregnanolone, the androgenic principle of human pregnancy urine.** R. E. Marker, O. Kamm, D. M. Jones, E. L. Wittle, T. S. Oakwood, and H. M. Crooks. **XIII. Dihydroequilenins.** R. E. Marker, O. Kamm, T. S. Oakwood, and F. H. Tendick (J. Amer. Chem. Soc., 1937, **59**, 614—616, 616—618, 619—621, 768, 768—769; cf. A., 1936, 1506).—VIII. Progesterone is correlated with androsterone (I) by conversion of *allo*pregnanedione into androstanedione (II). The former dione, m.p. 199—200°, obtained by CrO_3-oxidation of the mixture of pregnanediol and *allo*pregnanediol isolated from human urine, with H_2–PtO_2 in AcOH at 3 atm. gives (trans-)allo*pregnanediol*, m.p. 195—196°, the *diacetate*, m.p. 142—143°, of which with KOH–MeOH at 15—20° gives the 20-*monoacetate*, m.p. 170—171°. Oxidation of this with cold CrO_3–AcOH gives (trans-)allo*pregnan*-20-*ol*-3-*one acetate*, m.p. 156°. The derived (trans-)allo*pregnan*-20-*ol*-3-*one*, m.p. 195°, is dehydrated by $ZnCl_2$–AcOH and ozonised, yielding (II), m.p. 128° [also obtained with m.p. 132° from (I)], and a *substance*, m.p. 185°.

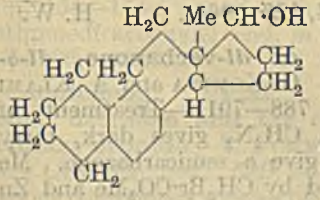
IX. The physiological action of sex hormones is probably accompanied by oxidation and/or reduction. 10,000 gals. of human pregnancy urine yielded no progesterone; it contained mostly pregnanediol and *allo*pregnanediol and epiallo*pregnan*-3-*ol*-20-*one* (I) (1—2 mg. per gal.), m.p. 162—164°, $[\alpha]_D^{30}$ +91° in EtOH (*acetate*, m.p. 139—140°, $[\alpha]_D^{30}$ +112° in EtOH; stable to Br; not pptd. by digitonin), oxidised by

CrO_3 to *allo*pregnanedione and hydrogenated (PtO_2) in AcOH to trans-epiallo*pregnane*-3 : 20-*diol*, m.p. 205—207° (*diacetate*, m.p. 124°). (I) is the first stage in reduction of progesterone. Urine is freed from theelol and theelin by Doisy's method; carbinols are then removed as Na phthalates; OH-ketones are removed from diols as sol. betainehydrazones; (I) is then purified as *semicarbazone*, m.p. 248—250° (decomp.).

X. Cholesteryl chloride and CrO_3–AcOH at 55° give a 25% yield of 7-*ketocholesteryl chloride* (I), m.p. 145° (*semicarbazone*, m.p. 176°), which with KOH in hot $Bu^{\alpha}CO_2H$ (no reaction in AcOH) gives 7-*ketocholesterylene*, m.p. 114° (obtained as sole product by KOH–EtOH), and *epi*cholesterol, and with H_2–PtO_2 in AcOH at 3 atm. affords a little α-cholestyl chloride (II) and 7-*hydroxycholestyl chloride* (III), an oil. Crude (III) with Na–C_5H_{11}·OH affords *cholestan*-7-*ol*, m.p. 117·5°, and with CrO_3 gives 7-*ketocholestyl chloride*, m.p. 139°. $Al(OPr^{\beta})_3$ and (I) give 7-*hydroxycholesteryl chloride*, m.p. 142° (*benzoate*, m.p. 119°), hydrogenated (PtO_2; 3 atm.) to a mixture of (II) and (III).

XII. *epiallo*Pregnan-3-ol-20-one (I), new m.p. 170°, is the androgenic principle of human pregnancy urine, being about as active (rat test) as androsterone. It is synthesised thus. By the carbinol degradation 3-chloro*allo*cholanic acid, m.p. 180°, affords successively its *Me* ester, m.p. 133°, the *diphenylcarbinol*, m.p. 171°, 3-*chloro*allo*norcholanic acid* (*Me* ester, m.p. 178°), the *diphenylcarbinol*, m.p. 183°, 3-*chlorobisnorcholanic acid*, m.p. 231° (*Me* ester, m.p. 150°), and the *diphenylcarbinol*, m.p. 146°. The last-mentioned carbinol is dehydrated, ozonised, and treated with KOH. The resulting (I) is purified by means of the H succinate and semicarbazone.

XIII. Equilenin and $Al(OPr^{\beta})_3$ give dihydroequilenin, m.p. 215° (benzoate, m.p. 204°), and its *epimeride*, m.p. 248° (*diacetate*, m.p. 124°; *benzoate*, m.p. 215°). Hydrogenation (PtO_2) is accompanied by dehydration, giving a 70% yield of a *substance* (annexed formula), $C_{18}H_{24}O$, m.p. 140° (*acetate*, m.p. 104°).



R. S. C.

Synthesis of the female ovarian hormone "folliculosterone." I. A. Remezov (Biochimia, 1937, **2**, 344—366; cf. Marker *et al.*, A., 1936, 1256).—The hormone (I), $C_{18}H_{22}O_2$, m.p. 248·0—248·5°, obtained by oxidation of the side-chain of neoergosterol, is probably 3-hydroxy-17-keto-5 : 7 : 9-œstratriene. 1 mg. of (I) is equiv. to 10,000 international units.

W. McC.

Simple preparation of the chloroketone, $C_{19}H_{27}OCl$, dehydroandrosteryl chloride. E. S. Wallis and E. Fernholz (J. Amer. Chem. Soc., 1937, **59**, 764—765).—This chloride, m.p. 154°, $[\alpha]_D^{22}$ +14·6° in $CHCl_3$, is obtained from dehydroandrosterone in 83% yield by PCl_5 in $CHCl_3$.

R. S. C.

Hormones of the androsterone group. N. D. Zelinski and M. I. Uschakov (Bull. Acad. Sci. U.R.S.S., 1936, 879—900).—A *semicarbazone*, $C_{27}H_{47}O_2N_3$, m.p. 221—223°, yielding a *hydroxyketone* (I), m.p. 175—177°, on hydrolysis, is obtained as a by-product of oxidation of ε-cholestanyl acetate. The probable structure of (I) is discussed. Dehydroandrosterone (II) and BzO_2H yield the 5 : 6-*oxide*, m.p. 228·5°, of (II), from which *androstane*-3 : 5 : 6-*triol*-17-*one*, m.p. 301—302°, is obtained.

R. T.

Separation of hydroxy-compounds of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1937, 393.

Isomerisation of $\Delta^{5:6}$-dehydroandrosterone and compounds derived therefrom.—See B., 1937, 393.

Tautomerism of benzoquinoneoxime–*p*-nitrosophenol systems. H. H. Hodgson (J.C.S., 1937, 520—527).—In part polemical against Anderson *et al.* (A., 1934, 527). The two bands in the absorption spectra of 3-halogenonitrosophenols (I) in aq. EtOH are due, respectively, to the anion $NO{\cdot}C_6H_3Cl{\cdot}O^-$ and the non-ionised mol., since they are eliminated by an excess of acid and of alkali, respectively. Similar conclusions apply to the two bands in the spectra of 3-halogenobenzoquinone-4-oximes (II) which are due to $O{:}C_6H_3Cl{:}NO^-$ and $O{:}C_6H_3Cl{:}N{\cdot}OH$, respectively. The differences between the absorption spectra of (I) and (II) are found in the widely different ε vals. for the two series. The following data are, respectively, the position of the band peak due to the ion (A.), its ε val., the band due to the non-ionised compound, and its ε val.: for (I), Cl, 4010, 1875, 2990, 6875; Br, 4015, 5625, 3040, 12,500; I, 4050, 9375, 3080, 12,500; for (II), Cl, 3990, 6875, 3030, 15,000; Br, 4015, 6250, 3040, 8750; I, 4030, 5625, 3080, 7500. Whereas the Cl-compounds of (I) and (II) possess considerable stability in acid and in alkaline solution, the Br- and I-compounds undergo immediate conversion into the more stable quinone monoximes. The Me ethers of (I) exhibit single absorption bands at about 3625 A., *i.e.*, between those of the mol. and ion forms of (I); the band of the Me ether of (II) is about 3200 A. (ε, approx. 12,000). The spectrum of 2-chloro-4-nitrosophenol (III) similarly consists of two bands at 3125 (ε, 6250) and 4125 A. (ε, 5625), which are suppressed by acids and alkalis, respectively, whereas the band of 2-chloro-4-nitrosoanisole is at 3500, and that of 2-chlorobenzoquinone-4-oxime Me ether is at 3300 A. Contrary to Anderson *et al.*, (III) is benzenoid in agreement with the author's earlier conclusion (A., 1932, 734) based on chemical evidence. Correlation between the spectra and electronic strain in the mol. is attempted.

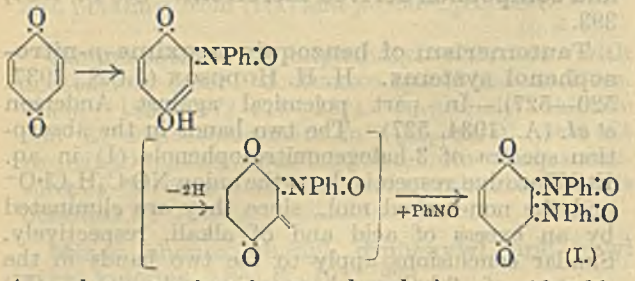
J. W. B.

Preparation and constitution of *cyclo*hexylammonium 2 : 5-di(*cyclo*hexylamino)-1 : 4-benzoquinone-3 : 6-disulphonate, 2 : 5-di(*cyclo*hexylamino)-1 : 4-benzoquinone, and quinol-2 : 5-disulphonic acid. (Mlle.) Y. Garreau (Compt. rend., 1937, **204**, 692—694).—Quinol, *cyclo*hexylamine, SO_2, and $Cu(OH)_2$ (cf. A., 1936, 721), or cyclo*hexylammonium quinol*-2 : 5-*disulphonate*, *cyclo*hexylamine, and $CuSO_4$, shaken in air, give cyclo*hexylammonium* 2 : 5-*di*(cyclo*hexylamino*)*benzoquinone*-3 : 6-*disulphonate*. This is hydrolysed by dil. acid to 2 : 5-*di*(cyclo*hexylamino*)*benzoquinone*, m.p. 242°,

of which the structure is established by prep. from benzoquinone, or 2 : 5-dianilinobenzoquinone, and *cyclo*hexylamine. From this, the 2 : 5-structure of quinol-2 : 5-disulphonic acid is confirmed.

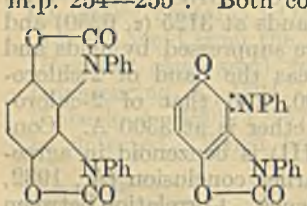
E. W. W.

Action of aromatic nitroso-compounds on quinones. W. Gündel and R. Pummerer (Annalen, 1937, **529**, 11—32).—Benzoquinone is slowly converted by PhNO in EtOH at room temp. or, less advantageously, in boiling EtOH–hexane into the corresponding 2 : 3-*dinitrone* (I), violent decomp. 179—180°. The course of the change is represented :



(I.)

Azoxybenzene is also produced in considerable quantity. (I) and Br in AcOH yield the *dibromide*. (I) is smoothly hydrogenated (Pt-sponge in C_6H_6) to 2 : 3-*dianilinoquinol* (II), m.p. 143—144° (decomp.), converted by Ac_2O at room temp. into the NN′-Ac_2 derivative, m.p. (indef.) 236—240° after darkening, and by exhaustive acetylation into the very unstable *benziminazolium* base [unstable *acetate* (III), m.p. 135—136° (decomp.); *picrate*, m.p. 207°; sparingly sol. *perchlorate*, m.p. 259°]. Conversion into the stable *ψ-base*, $(OAc)_2C_6H_2<^{NPh}_{NPh}>CMe{\cdot}OH$, m.p. 142—143°, is best effected by keeping (III) in contact with warm Et_2O. Treatment of (II) with $COCl_2$ in C_6H_6–PhMe containing $NPhMe_2$ at 100° gives the colourless, stable NN′-*diphenylbenzdioxazolone* (IV), sublimes at >300°; the anilinohydroxy-*N*-phenylbenzoxazolone produced in small amount is oxidised by $FeCl_3$ to the carmine-red *o-quinonephenylimine* (V), m.p. 254—255°. Both compounds give PhNC when boiled with aq. alkali. Hydrogenation of (II) in presence of feebly active Pt sponge affords 2-*anilino*-3-*phenylhydroxylaminoquinol*, which loses H_2O at 110° and forms 2 : 3-*dianilino*-p-*benzoquinone*, also obtained by oxidising (III) in Et_2O with PbO_2; it is transformed by NH_2Ph in EtOH containing AcOH into 2 : 3 : 5-*trianilino*-p-*benzoquinone*, which, like similar compounds obtained from other aromatic bases, dyes wool in clear yellow shades from a hyposulphite vat. *p*-Benzo- and tolu-quinone are transformed by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ into the corresponding *dinitrones*. The *dinitrones*, $C_{22}H_{20}O_4N_4Cl_2$ (+1C_6H_6 or +0·5 $CHCl_3$), violent decomp. 180—183°, and $C_{26}H_{24}O_4N_4$ are derived from 2 : 3-dichloro-*p*-benzoquinone and 1 : 4-naphthaquinone, respectively, whereas 1 : 2-naphthaquinone gives the *mononitrone*, $C_{18}H_{16}O_3N_2$, decomp. 180—200°. H. W.



Spectrochemical study of colours derived from quinoneimine.—See A., I, 217.

Action of hydroxylamine on quinizarin and its derivatives in alkaline medium. C. Marschalk (Bull. Soc. chim., 1937, [v], **4**, 629—636).—When heated with aq. NH_2OH quinizarin affords 2-*amino*-1 : 4-*dihydroxyanthraquinone* (I), m.p. 313—314°, identical with a specimen obtained by reduction of the NO_2-compound with $(NH_4)_2S$. Similarly Na quinizarin-2-sulphonate affords 3-*amino*-1 : 4-*dihydroxyanthraquinone*-2-*sulphonate*, and *Na* 1 : 4-*dihydroxyanthraquinone*-2 : 3-*dicarboxylate* is converted into 2-*amino*-1 : 4-*dihydroxyanthraquinone*-3-*carboxylic acid*. The formation of these products probably involves addition of NH_2OH to the quinizarin 2 : 3-double linking followed by an intramol. reduction, since alizarin and 2-hydroxyanthraquinone with NH_2OH give products from which the original components are regenerated by hydrolysis with 20% HCl at 250°. (I) is converted by glycerol–H_2SO_4–$PhNO_2$ into 2 : 3-*pyridino*-1 : 4-*dihydroxyanthraquinone* from which acid browns may be obtained by condensation with aromatic amines in presence of H_3BO_3 and sulphonation of the resulting NH_2-compounds.

J. W. B.

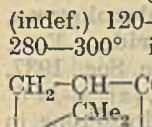
Manufacture of [higher] alkoxyanthraquinones.—See B., 1937, 328.

Manufacture of 2-aminoquinazarin and substitution products thereof.—See B., 1937, 328.

Investigation of catalytic racemisation with deuterium as indicator. H. Erlenmeyer, H. Schenkel and A. Epprecht (Helv. Chim. Acta, 1937, **20**, 367—368; cf. this vol., 18).—Catalytic racemisation of *l*-menthyl *d*-phenylbromoacetate by KOEt in EtOD gives a product containing D and thus supports the scheme of racemisation advanced by McKenzie (J.C.S., 1924, **125**, 1066). H. W.

Complete synthesis of *dl*-verbanone, *dl*-δ-pinene, and *dl*-pinane. G. Komppa and A. Klami (Ber., 1937, **70**, [*B*], 788—791).—Treatment of pinononyl chloride with CH_2N_2 gives dark, tarry matter which does not give a semicarbazone. Me pinononate is transformed by $CH_2Br{\cdot}CO_2Me$ and Zn filings in C_6H_6 into *Me*$_2$ *hydroxy*iso*homopinocamphorate*, $CO_2Me{\cdot}CH<^{CH_2}_{CMe_2}>CH{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Me$, b.p. 170—175°/11 mm., dehydrated by $SOCl_2$ and then hydrolysed to *dehydro*iso*homopinocamphoric acid* (I), m.p. 194°, which is oxidised by $KMnO_4$ to *dl*-pinononic acid. (I) is reduced (PtO_2 in AcOH) to iso*homopinocamphoric acid*

$CO_2H{\cdot}CH<^{CH_2}_{CMe_2}>CH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, m.p. (indef.) 120—135°, the *Pb* salt of which passes at 280—300° into dl-*verbanone* (II) (*semicarbazone*, m.p. 218°), identical with that obtained by hydrogenation (PtO_2 in EtOH) of *dl*-verbenone. Removal of H_2O from *dl*-verbanol by $SOCl_2$ in C_5H_5N gives *dl*-δ-pinene, b.p. 157—159°/771 mm., oxidised by alkaline $KMnO_4$ to *dl*-pinocamphoric acid, m.p. 185—186°. H. W.



(II.)

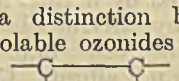
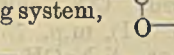
Structure of *iso*borneol. I. New isomeride of borneol. V. N. KRESTINSKI and A. ESCHTSCHENKO. **II. Velocity of esterification of isomeric dicyclic alcohols of the camphor, camphene, and fenchyl series.** V. N. KRESTINSKI, M. NEMILOV, and I. BARDISCHEV (J. Gen. Chem. Russ., 1937, 7, 415—422, 423—429).—I. Achmatowicz's results (A., 1927, 250; 1928, 645) are confirmed.

II. The velocity coeffs. of acetylation of borneol, *endo*borneol, and fenchyl and *iso*fenchyl alcohol are of the same order of magnitude (0·0111—0·0117), and differ from those of *iso*borneol, camphene hydrate, and methylcamphenilol (0·00767—0·00779); it is concluded that the members of the respective groups have the same general structure. R. T.

Preparation of bornyl chloride. E. N. ROSTOVSKI and V. SCHEREMETEVA (Plast. Massui, 1935, No. 3, 33—34).—Pinene is saturated with HCl at 90°.

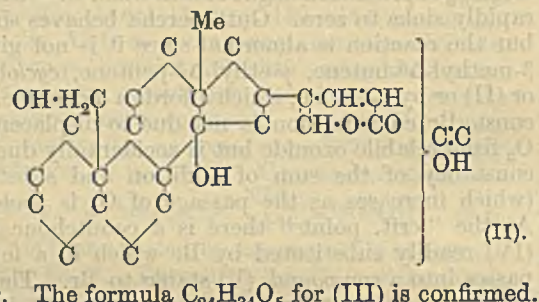
CH. ABS. (*r*)

Totarol. I. W. F. SHORT and H. STROMBERG (J.C.S., 1937, 516—520).—Totarol (I), $C_{20}H_{30}O$, m.p. 132°, $[\alpha]_D^{20}$ +41·34° in EtOH, gives a *formate*, m.p. 125·5°, *acetate*, m.p. 121·5°, $[\alpha]_D^{18}$ +44·58° in Et_2O, *H phthalate*, m.p. 161—163°, and *Me ether*, m.p. 92—92·5°, $[\alpha]_D^{18}$ +41·95° in Et_2O. H_2–Pd reduces (I) with difficulty to *totarane* (II), m.p. 74·5—75°, $[\alpha]_D^{20}$ −31·06° in Et_2O, and *dihydrototarol*, m.p. 151—151·5°, $[\alpha]_D^{20}$ +20·13° in Et_2O (*formate*, m.p. 104·5—105°), which is further reduced to *tetrahydrototarol*, m.p. 134·5°. Dehydrogenation of (I) with Se or Pd–C affords C_3H_8 and 7-*hydroxy*-1-*methylphenanthrene*, m.p. 190—191°, which forms a *Me ether*, m.p. 133·5—134·5°, and an *acetate*, m.p. 133·5—136°, oxidised to a *quinone*, m.p. 207° (decomp.) [*quinoxaline*, m.p. 244·5—245·5°; corresponding *OH-quinone*, m.p. 228° (decomp.)]. Pd–C dehydrogenates (II) to a *hydrocarbon*, $C_{18}H_{18}$, m.p. 101·5—102° (*picrate*, m.p. 142·5°), oxidised with CrO_3 to a *quinone*, m.p. 160·5—161·5° (*quinoxaline*, m.p. 154—154·5°), and with $K_3Fe(CN)_6$ to a phenanthrenedicarboxylic acid, m.p. 200—206° (Me ester, m.p. 135·5—136°). F. R. S.

Caoutchouc. XVIII. The various caoutchouc ozonides and the existence of Harries' primary ozonide. R. PUMMERER and H. RICHTZENHAIN (Annalen, 1937, 529, 33—67).—Examination of various compounds which appear to indicate a relative stability of primary ozonides as defined by Harries gives no confirmation of their existence. It is therefore unnecessary to draw a distinction between ozonides and *iso*ozonides. Isolable ozonides do not contain the Harries ring system,  , but the arrangement  proposed by Staudinger for *iso*ozonides. The formation of polymeric ozonides is best explained by Staudinger's assumption of the primary formation of "molozonides," which are regarded as a very unstable, intermediate phase. The action of heat on mesityl oxide ozonide (I) gives only $COMe_2$ and its peroxide, AcCHO, AcOH, and HCO_2H; unchanged mesityl oxide (II) could not be detected with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2. Cautious reduction of (I) with quinol, NHPh·NHPh, Al–Hg, or Zn dust + $AgNO_3$ does not appear to give α-acetyl-β-methylpropane-αβ-diol, which can readily be identified by conversion in 17% H_2SO_4 into the 2 : 4-*dinitrophenylhydrazone*, m.p. 164—166° (decomp.). (An apparatus for the reduction of an ozonide immediately after its formation is described.) Fumaric acid does not appear to react with O_3 in EtOAc at −70° and the "acid recovered from the ozonide" by Harries was probably unattacked material. Et_2 fumarate in CCl_4 yields the *ozonide*, m.p. 42—43°, which does not reform the ester when preserved; when obtained in EtOAc at −55° and immediately reduced by Al–Hg it yields only CHO·CO_2Et without sign of a molozonide convertible into Et_2 tartrate. Ozonisation of dihydrodi*cyclo*pentadiene in EtOAc at −75° gives an *ozonide*, m.p. 60—62°, which, unlike Staudinger's product, m.p. 125—130°, obtained in CCl_4, is readily sol. in Et_2O; it is scarcely affected by H_2–Pt–SiO_2 at 0° or 20° and liberates I very slowly from HI. More drastic fission by Zn and AcOH leads normally to 3 : 6-endo*methylenehexahydrohomophthaldialdehyde*, b.p. 112°/0·3 mm. [*di*-2 : 4-*dinitrophenylhydrazone*, m.p. 212° (decomp.); (?) *disemicarbazone*, m.p. 189°], which becomes polymerised when preserved. Titration of solutions of caoutchouc (III) with Br during ozonisation indicates a constancy of Br absorption until O_3 is present in slight excess when the absorption rapidly sinks to zero. Guttapercha behaves similarly but the reaction is abnormal since it is not given by β-methyl-Δ^β-butene, γ-ethyl-Δ^β-pentene, *cyclo*hexene, or (II) or by β-ionone, which affords a diozonide. The const. Br consumption is not due to displacement of O_3 from a labile ozonide but is accidentally due to the constancy of the sum of addition and substitution (which increases as the passage of O_3 is prolonged). At the "crit. point" there is a caoutchouc *ozonide* (IV) readily substituted by Br which in a few min. passes into a *compound* (V) stable to Br. The latter material gives β-bromo- and some βδ-dibromo-lævulic acid when reduced with SO_2. Pyridine dibromide hydrobromide is preferable to Br for the titration of (III). Caoutchouc oxide (V), from (III) and BzO_2H, is stable to Br and mixtures of (III) and (VI) in $CHCl_3$ behave normally with Br until the double linkings are saturated. (IV) and (V) are $(C_5H_8O_3)_n$ and do not differ appreciably from one another in physical and chemical properties except with regard to behaviour towards Br; (V) is stable whereas (IV) absorbs varying amounts of Br reaching 91% of that required by the parent (III). In $CHCl_3$ (IV) appears to remain unchanged during 14 days at 0° whereas (V) gives rise to lævulic acid peroxide. Attempts to transform (IV) into a polyglycol $[\cdot CH_2\cdot CMe(OH)\cdot CH(OH)\cdot CH_2\cdot]_n$ by cautious reduction with Al–Hg were unsuccessful. Among other reagents, only BzO_2H resembles O_3 in its action towards the sensitiveness of (IV) to Br. Similarly it restricts the bromination of $COMe_2$ and $CH_2Ac\cdot CO_2Et$. It appears therefore that the final quantities of O_3 are adequate to produce so much caoutchouc ozonide peracid as is necessary to inhibit substitution by Br: inhibition is most probably due to destruction of HBr. In presence of HBr, $COMe_2$ immediately decolorises Br, much less rapidly in its absence. BzO_2H in indifferent media oxidises HBr to Br immediately. Passage of O_3 through (III) in CCl_4

causes spontaneous separation of a new *ozonide* (VI) which softens at 85° and is more sparingly sol. in the usual media than that obtained in $CHCl_3$. When a deficiency of O_3 is employed essentially (VI) is produced whilst some (III) remains unchanged. The mol. wt. of (VI) in $CHBr_3$ agrees with $(C_5H_8O_3)_5$ but other properties suggest that it is degraded in this solvent. (VI) has little activity towards HI or Br. H. W.

Toad poisons. Chemical constitution of marinobufagin, cinobufagin, and gamabufagin. H. JENSEN (J. Amer. Chem. Soc., 1937, **59**, 767—768).—Cinobufagin (I) and Se give the Diels hydrocarbon, $C_{18}H_{16}$. Marinobufagin (II) and (I) contain 3 ethylenic linkings, since hydrogenation affords α-, m.p. 212—213°, and β-*hexahydromarinobufagin*, m.p. 225—227°, and α-, m.p. 230—232°, and β-*hexahydrocinobufagin*, m.p. 210—212°, with small amounts of acids. Ozonisation of (I) or (II) gives HCO_2H, $CHO{\cdot}CO_2H$, and $H_2C_2O_4$. (I) and gamabufagin (III) contain $CH_2{\cdot}OH$ attached to $C_{(10)}$ or $C_{(13)}$ (corresponding to the *ang.*-Me of the sterols), which is eliminated as CH_2O by strong acids or alkalis and is oxidised to CHO by CrO_3. Acid removes 2 OH as H_2O from (II) and 1 OH from (III). The following structure is suggested for (II); (I) and (III) are probably



(II).

similar. The formula $C_{24}H_{34}O_5$ for (III) is confirmed. (III) has only two ethylenic linkings, both in the lactone ring. R. S. C.

Manufacture of hydroxy[coumaran]carboxylic acids and of amides derived therefrom.—See B., 1937, 421.

Geometrical inversion in acids derived from coumarins. IV. Behaviour of the ethers of *cis*- and *trans*-acids. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, **5**, **A**, 249—256).—The interconversion of the *cis*- and *trans*-acids (improved preps.) from coumarin, 7-methyl- and 6-nitro-coumarin with HCl–EtOH, H_2SO_4, and HgO in neutral, acidic, and alkaline media shows the *trans*-form to be favoured. With conc. H_2SO_4, hydrolysis of the ether and ring-closure take place. The following are described: 4-*methylcoumarinic acid Me ether*, m.p. 160—161°, from 7-methylcoumarin in MeOH with MeI and NaOMe, and 4-*methylcoumaric acid Me ether*, m.p. 209—210°, from the OH-acid and Me_2SO_4. J. D. R.

Natural coumarins. XXV. Fraxinol, a new component of ash bark. E. SPÄTH and Z. JERZMANOWSKA-SIENKIEWICZOWA (Ber., 1937, **70**, [*B*], 698—702).—Extraction of the (necessarily) fresh bark of *Fraxinus excelsior*, L., with Et_2O and treatment of the extracts with MeOH and H_2O followed by hydrolysis affords *fraxinol* [6-*hydroxy*-5:7-*dimethoxycoumarin*] (I), m.p. 171—172° [*Ac* derivative (II), m.p. 140—141°; *Me* ether, b.p. 160°/0·1 mm., m.p. 76—77°]. 2:6-Dimethoxy-*p*-benzoquinone, m.p. 255° (decomp.), is reduced by $SnCl_2$ and HCl to 2:6-*dimethoxyquinol*, m.p. 166—167° (vac.), converted by $Zn(CN)_2$ and HCl in Et_2O into 3:6-*dihydroxy*-2:4-*dimethoxybenzaldehyde*, m.p. 141—142° (vac.). This is transformed by anhyd. NaOAc and Ac_2O into (II), hydrolysed to (I), identical with the natural product. H. W.

Natural coumarins. XXVI. Constitution and synthesis of ayapin. E. SPÄTH, P. K. BOSE, and J. SCHLÄGER (Ber., 1937, **70**, [*B*], 702—704).—Exhaustive extraction of the dried leaves of *Eupatorium Ayapana*, Vent., with light petroleum of low b.p. and treatment of the dry extract with boiling H_2O followed by Et_2O leads to ayapanin, m.p. 119° (J.C.S., 1910, **97**, 1131), and *ayapin* [6:7-*methylenedioxycoumarin*] (I), m.p. 231—232° (vac.). (I) is hydrolysed by H_2SO_4 and phloroglucinol to æsculetin (II) (identified as the Me_2 ether) and obtained synthetically from (II), CH_2I_2, and NaOMe in MeOH. H. W.

Syntheses in the 5-hydroxybenzopyrone group. II. 5-Hydroxy-4-methylcoumarin. D. B. LIMAYE and G. R. KELKAR (Rasāyanam, 1936, **1**, 45—48; cf. this vol., 257).—The substance, m.p. 263°, obtained in poor yield with chromones from 2-acetylresorcinol and Ac_2O–NaOAc (A., 1935, 854) is 5-*hydroxy*-4-*methylcoumarin* (*Ac* derivative, m.p. 114°; no $FeCl_3$ colour), since it or its *Me ether* (I), m.p. 143°, when boiled with *N*-NaOH and then shaken with Me_2SO_4, gives 2:6-*dimethoxy*-β-*methylcinnamic acid*, m.p. 185°. Hydrolysis without subsequent methylation gives a very poor yield of 2:6-$(OH)_2C_6H_3{\cdot}CMe{:}CH{\cdot}CO_2H$, but the $(OMe)_1$-acid could not be obtained from (I) owing to instantaneous ring-closure. R. S. C.

Synthesis of 6-hydroxy-7-acylcoumarones. I. 6-Hydroxy-7-acetyl-3-methylcoumarone. D. B. LIMAYE and N. R. SATHE (Rasāyanam, 1936, **1**, 48—59).—Hydrolysis of 3-*bromo*-7-*hydroxy*-8-*acetyl*-4-*methylcoumarin* (I), m.p. 218° (*semicarbazone*, m.p. >275°; *Ac* derivative, m.p. 226°, degraded by hot alkali), obtained from 8-acetyl-4-methylumbelliferone by Br–AcOH, is abnormal, but its structure is proved by normal hydrolysis of its *Me ether*, m.p. 187°, by 2*N*-NaOH to 7-*acetyl*-6-*methoxy*-3-*methylcoumarilic acid*, m.p. 234° (decomp.), which above the m.p. affords CO_2 and 7-*acetyl*-6-*methoxy*-3-*methylcoumarone* (II), m.p. 75° (*semicarbazone*, m.p. 206°). With hot *N*-NaOH (I) gives 6-*hydroxy*-7-*acetyl*-3-*methylcoumarilic acid* (III), m.p. 252° (decomp.) [obtained as sole product by 10*N*-NaOH; mixed *anhydride* with AcOH, m.p. 87°; *Et*, m.p. 103°, and *Me* ester, m.p. 156° (*Me ether*, m.p. 132°); with Me_2SO_4 gives (II); *Bz* derivative, m.p. 113°], 6-*hydroxy*-7-*acetyl*-3-*methylcoumarone* (IV), m.p. 112°, b.p. 290—292° [formed from (III) by loss of CO_2 and also obtained from (I) and hot 7% Na_2CO_3 or from (II) by $AlCl_3$; *semicarbazone*, m.p. 227° (decomp.)], and a *substance* (V), $C_{11}H_{10}O_3$, m.p. 99°; with hot 3*N*-NaOH it gives an *acid*, $C_{12}H_{10}O_5$, m.p.

143° (decomp.) (*Me* ester, m.p. 88°; *Me ether*, m.p. 150°; *semicarbazone*), which gives CO_2 and (IV). Ac_2O–NaOAc converts (III) at 160—165° into 6-hydroxy-3-methylcoumarone, m.p. 103°, the *acetate*, m.p. 58°, of which with $AlCl_3$ at 120—130° gives (IV) and a *substance*, m.p. 190°. Under other conditions (not detailed) (I) gives a *phenol*, m.p. 91°, converted by dehydration into a *substance*, m.p. 120°, both of which with hot acid give (V). R. S. C.

Constitution of nitro-β-methylumbelliferone methyl ether and of chlororesorcinol. D. Chakravarti and B. C. Banerji (J. Indian Chem. Soc., 1937, **14**, 37—38).—The isomeride of 8-nitro-7-methoxy-4-methylcoumarin, also formed during the nitration of β-methylumbelliferone Me ether, is identified as 6-*nitro*-7-*methoxy*-4-*methylcoumarin* (I), m.p. 281°, since it is demethylated to 6-*nitro*-7-*hydroxy*-4-*methylcoumarin*, m.p. 253°, also obtained, m.p. 255°, by condensation of 4-nitroresorcinol with $CH_2Ac{\cdot}CO_2Et$. (I) is converted, through the 6-NH_2-compound, into 6-*chloro*-7-*methoxy*-4-*methylcoumarin*, m.p. 252°, also obtained from the 7-OH-compound (A., 1935, 1504) derived from 4-chlororesorcinol, the structure of which (cf. A., 1936, 858) is thus confirmed. E. W. W.

Effect of methylation on the course of hydrolysis of 8-acetyl-4-methylumbelliferone by caustic alkali. Formation of stable *cis*- and *trans*-2-hydroxy-4-methoxy-3-acetyl-β-methylcinnamic acids. D. B. Limaye and N. R. Sathe (Rasāyanam, 1936, **1**, 30—38).—8-Acetyl-4-methylumbelliferone (I) (A., 1932, 521) with Me_2SO_4–NaOH gives 7-*methoxy*-8-*acetyl*-4-*methylcoumarin*, m.p. 137° (*semicarbazone*, m.p. 254°), which with boiling *N*-NaOH gives cis-2-*hydroxy*-4-*methoxy*-3-*acetyl*-β-*methylcinnamic acid* (II), m.p. 163° (decomp.), readily reconverted into (I). (II) is methylated to cis-2 : 4-*dimethoxy*-3-*acetyl*-β-*methylcinnamic acid* (III), m.p. 157—158°, and its *Me* ester, m.p. 95—97°. As a by-product with (II), 2-*hydroxy*-6-*methoxy*-3-iso*propenylacetophenone* (IV), m.p. 61°, is formed, converted by dil. acids into a *substance*, m.p. 204°. With Me_2SO_4, (IV) yields the 2 : 6-*dimethoxy*-compound, b.p. 279—280° (*semicarbazone*, m.p. 168°), also obtained from (III) at 200°. A further by-product with (II) is trans-2-*hydroxy*-4-*methoxy*-3-*acetyl*-β-*methylcinnamic acid* (V), m.p. 175° [converted above its m.p. into (IV)], which with Me_2SO_4 gives the 2 : 4-*dimethoxy*-acid, m.p. 132°, without ester. (I) with NaOEt–EtOH, followed by HCl, gives (V), also obtained from (II) or (III) and aq. NaOH. E. W. W.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds. III. Action of mercuric acetate on coumarinic and coumaric acids and esters. P. S. Rao and T. R. Seshadri (Proc. Indian Acad. Sci., 1936, **4**, A, 630—638; cf. A., 1936, 997, 1516).—Coumarinic acid with $Hg(OAc)_2$–H_2O gives 3 : 5 : α-*triacetoxymercuri*-β-*acetoxymelilotic acid*, decomp. at 245° (cf. Naik *et al.*, A., 1934, 1107), which with NaOH–H_2O gives 3 : 5-diacetoxymercuricoumaric acid (cf. A., 1930, 913). 5-Nitrocoumarinic acid gives 5-*nitro*-α-*acetoxymercuri*-β-*acetoxymelilotic acid*, decomp. at 170°, converted by NaOH–H_2O into 5-nitrocoumaric acid (I) (cf. *locc. cit.*). Coumaric acid (II) when refluxed with $Hg(OAc)_2$–MeOH gives 3 : 5 : α-*triacetoxymercuri*-β-*methoxymelilotic acid*, m.p. 234° (decomp.) [*Me* ester (III), decomp. at 265°, obtained similarly from the Me ester of (II)], converted by H_2S in NaOH into β-methoxymelilotic acid, and by successive treatment with Br–AcOH and KOH–EtOH into 4 : 6-dibromocoumarilic acid, obtained likewise from (III). By similar methods (I) yields 5-*nitro*-3 : α-*diacetoxymercuri*-β-*methoxymelilotic acid*, turns grey at 258° (*Me* ester, decomp. at 238°), converted into (I) by H_2S in NaOH and into 6-*bromo*-4-*nitrocoumarilic acid*, m.p. 252—253°, by successive treatment with Br–AcOH and KOH–H_2O, and 4-methylcoumaric acid yields 3 : 5 : α-*triacetoxymercuri*-4-*methyl*-β-*methoxymelilotic acid*, m.p. 228° (decomp.) (*Me* ester, m.p. about 284°), converted by bromination and subsequent treatment with KOH–H_2O into 4 : 6-*dibromo*-5-*methylcoumarilic acid*, m.p. 270°. The coumarilic acids were also obtained from the appropriate bromocoumarins. H. G. M.

Reaction between quinones and sodium enolates. V. 2 : 3-Dimethylnaphthoquinone and sodiomalonic ester. L. E. Smith and (Miss) I. M. Webster. **VI. Duroquinone and sodioacetoacetic ester.** L. E. Smith and D. Tenenbaum. **VII. Bromo-ψ-cumoquinone and sodiomalonic ester.** L. E. Smith and K. C. Johnson (J. Amer. Chem. Soc., 1937, **59**, 662—667, 667—672, 673—679; cf. A., 1936, 732).—V. 2 : 3-Dimethyl-1 : 4-naphthoquinone (I) (modified prep.) and $CHNa(CO_2Et)_2$ in Et_2O–EtOH, best when stirred in air, give a Na compound, which with HCl gives 6-*hydroxy*-3-*carbethoxy*-5-*methyl*-α-*naphthocoumarin* (II), m.p. 212—213°, the structure of which is proved by the reactions given below. Thus (I) reacts in the same way as does duroquinone. The yellow colour of the derivatives of (II) makes it unnecessary to postulate a special formula to account for colours of coumarin derivatives. With H_2–Pd in EtOH or MeOH at about 1·2 atm. (II) gives 6-*hydroxy*-3-*carbethoxy*-5-*methyl*-3 : 4-*dihydro*-α-*naphthocoumarin* (III), m.p. 175—176° (*Ac* derivative, m.p. 145—145·5°). Hydrolysis of (II) by most reagents causes decomp., but HCl in aq. $COMe_2$ gives 6-*hydroxy*-3-*carboxy*-5-*methyl*-α-*naphthocoumarin* (IV), m.p. 275—276° (decomp.; bath preheated to 240°), 263° (decomp.; no preheating) [*Ac* derivative, m.p. 258° (decomp.), gives oils when hydrogenated], hydrogenation of which gives mixtures of the carboxydihydrocoumarin and decarboxylated dihydrocoumarin, which could not be isolated owing to the ease of oxidation; hydrolysis of (III) gives small amounts of a substance, m.p. 155—159°, probably the corresponding *acid*, and a substance, m.p. 120—125°, probably 6-*hydroxy*-5-*methyl*-α-*naphthocoumarin*. (II), its yellow *Ac* derivative, m.p. 195—196°, or (IV) with Me_2SO_4–KOH in hot aq. MeOH gives 3-*carboxy*-6-*methoxy*-5-*methyl*-α-*naphthocoumarin* (V), m.p. 222—225°, also obtained by other methods; under restricted conditions, (II), NaOMe, and Me_2SO_4 give 3-*carbethoxy*-6-*methoxy*-5-*methyl*-α-*naphthocoumarin*, m.p. 182—183°, also obtained impure when the Na derivative from the original condensation is heated with MeI

in MeOH; with 10% KOH it gives the mono-ether (V). (II) and CH_3N_2 give a *substance*, m.p. 138—139°. Reduction of (I) by Zn dust leads to 1 : 4-*diacetoxy*-2 : 3-*dimethylnaphthalene*, m.p. 189—190°, or the unstable *quinhydrone*, m.p. 139—144° (also obtained in the coumarin condensation in absence of O_2). 2 : 1 : 4-$C_{10}H_5Me(OAc)_2$, m.p. 112·5—114°, is obtained from 2-methyl-1 : 4-naphthoquinone, but neither the free quinol nor its Me_2 ether could be obtained; the quinhydrone (prep. by Pd-hydrogenation in dry Et_2O at 1·34 atm.) with HCl and $Zn(CN)_2$ in Et_2O gives 64% of 1 : 4-*dihydroxy*-3-*methyl*-2-*naphthaldehyde*, m.p. 158—160°, which with $CH_2(CO_2Et)_2$ and piperidine in EtOH gives (II) and in AcOH the Ac derivative of (II) and with $CH_2(CO_2H)_2$ and piperidine in MeOH gives (IV).

VI. Duroquinone reacts with CHNaAc·CO_2Et in C_6H_6 as with $CHNa(CO_2Et)_2$, yielding 0·5 mol. of the quinol and 0·5 mol. of a Na compound, which with HCl affords 6-*hydroxy*-3-*acetyl*-5 : 7 : 8-*trimethylcoumarin* (I), m.p. 227—228° (*Bz* derivative, m.p. 162—163°), the structure of which is proved by the reactions given below. Hydrogenation (Pd; EtOH; 3 atm.) of (I) gives 6-*hydroxy*-3-*acetyl*-5 : 7 : 8-*trimethyl*-3 : 4-*dihydrocoumarin*, m.p. 164—165° {*Ac* derivative, m.p. 124—125°, and *Me ether* (II), m.p. 112—113·5° [*oxime*, m.p. 156—157° (decomp.)], also obtained by hydrogenation of the *Ac* derivative, m.p. 201—202·5°, and *Me ether* (III) (prep. only from the solid Na derivative and Me_2SO_4 in MeOH, m.p. 158·5—159·5°; *benzylidene* derivative, m.p. 187—189°), of (I); *oxime*, m.p. 179—180° (decomp.)}. Dimethoxyduraldehyde and CHNaAc·CO_2Et in MeOH give *Et* 2 : 5-*dimethoxy*-3 : 4 : 6-*trimethylbenzylidene-acetoacetate*, an oil, from which (I) is obtained by boiling first with 10% KOH–EtOH and then with HI. Oxidation of (I) or (III) usually causes degradation, but the Na derivative of (I) with Br gives $CHBr_3$ and a little 6-hydroxy-3-carboxy-5 : 7 : 8-trimethylcoumarin. The *oxime*, m.p. 258—260° (decomp.), of (I) did not undergo Beckmann rearrangement without decomp., but the *oxime*, m.p. 225—227° (decomp.), of (III) with $PhSO_2Cl$ in C_5H_5N at room temp. gives 3-*acetamido*-6-*methoxy*-5 : 7 : 8-*trimethylcoumarin*, m.p. 237—238°, hydrolysed by 6*N*-HCl to the *amine*, m.p. 150—151°. 3-Carboxy-6-methoxy-5 : 7 : 8-trimethylcoumarin gives (*a*) the *methylamide*, m.p. 214—215°, (*b*) the *azide*, m.p. about 210° (violent decomp.), which could not be degraded by acid, and (*c*) a *hydroxamic acid*, m.p. 236—237°, unchanged by Ac_2O–$COMe_2$.

VII. In accordance with an electronic interpretation *bromo-ψ-cumoquinone* (I) reacts with $CHNa(CO_2Et)_2$ in Et_2O, EtOH, or, less well, C_6H_6, by 1 : 4-addition to give a Na compound, decomposed by acid to 8-*bromo*-6-*hydroxy*-3-*carbethoxy*-5 : 7-*dimethylcoumarin* (II), m.p. 200°, the structure of which is proved by the reactions described below and by synthesis of derivatives. 5-Bromo-ψ-cumene in $CHCl_3$ with H_2SO_4–HNO_3 (*d* 1·5) gives the 3 : 6-$(NO_2)_2$-derivative (93% yield), new m.p. 221—222°, reduced ($SnCl_2$) to 5-*bromo*-3 : 6-*diamino*-ψ-*cumene*, m.p. 155° (decomp. from 150°), the stannichloride of which with $FeCl_3$ affords (I), m.p. 79—80° (*quinhydrone*, m.p. 148·5—149·5°), reduced by $SnCl_2$ to *bromotrimethylquinol*, m.p. 185° (decomp. from 170°) (*Me_2 ether*, m.p. 71—72°; *Ac_2*, m.p. 178—179°, and *Bz_2* derivative, m.p. 253—255°). (II) (*Ac* derivative, m.p. 160—161°) with HCl gives 8-*bromo*-6-*hydroxy*-3-*carboxy*-5 : 7-*dimethylcoumarin* (III), m.p. 250° [*Ac* derivative, (IV), m.p. 223°; *Me ether*, m.p. 210°, obtained by KOH–MeOH–Me_2SO_4 from (II), (III), or (IV)], and is debrominated by H_2–Pd in EtOH at 2·8 atm. to yield 6-*hydroxy*-3-*carbethoxy*-5 : 7-*dimethyl*-3 : 4-*dihydrocoumarin* (V), m.p. 142—143°. *p*-Xyloquinone (modified prep.), new m.p. 124—125°, gives the quinol, m.p. 215—216°, the Me_2 ether, new m.p. 110—111°, of which with $Zn(CN)_2$–HCl–C_6H_6 gives 3 : 6-*dimethoxy*-2 : 5-*dimethylbenzaldehyde*, m.p. 59—60° (*oxime*, m.p. 118—119°); this did not yield a homogeneous Br-derivative; with $CH_2(CO_2H)_2$ it gives 3 : 6-*dimethoxy*-2 : 5-*dimethylbenzylidenemalonic acid*, m.p. 195° (evolution of CO_2; after resolidification melts at about 215°), or on long heating 3-*carboxy*-6-*methoxy*-5 : 8-*dimethylcoumarin*, m.p. 229—230°, also obtained by fusion of the malonic acid. *m*-Xyloquinone (prep. from mesidine), m.p. 74—75°, gives similarly 3 : 6-*dimethoxy*-2 : 4-*dimethylbenzaldehyde*, m.p. 145°, which with $CH_2(CO_2H)_2$ and piperidine in cold EtOH (3 days) gives 6-*hydroxy*-3-*carboxy*-5 : 7-*dimethylcoumarin*, m.p. 235—236° [is not smoothly debrominated; also obtained from (V) by $FeCl_3$], the *Et* ester, m.p. 165—166° [could not be obtained from the aldehyde by $CH_2(CO_2Et)_2$], of which is hydrogenated to (V). $CH_2(CO_2Et)_2$, (I), and $Mg(OEt)_2$ in EtOH give a Mg compound, which with HCl affords (II), but with Me_2SO_4 in MeOH yields 3-*bromo*-5-*hydroxy*-2-*methoxy*-4 : 6-*dimethylbenzylidenemalonic acid*, m.p. 240—241° [unchanged by HCl–$COMe_2$; gives (III) with HBr–AcOH; with Ac_2O–H_2SO_4 gives a *substance*, m.p. 187—188°), and with pure AcCl affords 3-*bromo*-5-*hydroxy*-2-*acetoxy*-4 : 6-*dimethylbenzylidenemalonic acid*, m.p. 231—232°, converted by Me_2SO_4–KOH–MeOH into the Me ether of (III).

R. S. C.

Heterocyclic compounds. I. Coumarins from 2-carbethoxy*cyclo*pentanone and 2-carbethoxy-4-methyl*cyclo*pentanone. S. Z. Ahmad and R. D. Desai (Proc. Indian Acad. Sci., 1937, 5, A, 277—284).—2-Carbethoxy*cyclo*pentanone (I), H_2SO_4, and PhOH yield cyclo*penteno*-1′ : 2′ : 4 : 3-*coumarin*, m.p. 129°. Similarly, the following are prepared: from *p*-cresol, 6-*methyl*-, m.p. 173—174°, from *m*-cresol, 7-*methyl*-, m.p. 247°, from resorcinol, 7-*hydroxy*- (II), m.p. 247° (*acetate*, m.p. 158—159°; *benzoate*, m.p. 166—167°), from 4-ethylresorcinol, 7-*hydroxy*-6-*ethyl*-, m.p. 266° (*acetate*, m.p. 168°), -cyclo*penteno*-1′ : 2′ : 4 : 3-*coumarin*. Similarly, with (I) and $POCl_3$, 4 : 6-diethylresorcinol yields 5-*hydroxy*-6 : 8-*diethyl*-, m.p. 195°, orcinol, 5-*hydroxy*-7-*methyl*-, m.p. 253—254° (*acetate*, m.p. 139—140°), phloroglucinol, 5 : 7-*dihydroxy*- (III), m.p. 273° (*diacetate*, m.p. 140°), and pyrogallol, 7 : 8-*dihydroxy*-, m.p. 270° (*diacetate*, m.p. 194°), -cyclo*penteno*-1′ : 2′ : 4 : 3-*coumarin*. (I) and α-$C_{10}H_7$·OH with H_2SO_4 afford cyclo*penteno*-1′ : 2′ : 4 : 3-α-*naphthapyrone*, m.p. 218°. With 2-carbethoxy-4-methyl*cyclo*pentanone and H_2SO_4, resorcinol yields 7-*hydroxy*- (IV), m.p. 173° (*acetate*, m.p. 143—144°), and 4-ethylresorcinol, 6-*ethyl*-7-*hydroxy*- (V), m.p. 198° (*acetate*, m.p. 116°), -4′-

*methyl*cyclo*penteno*-1′ : 2′ : 4 : 3-*coumarin*, whilst α-$C_{10}H_7$·OH affords 4′-*methyl*cyclo*penteno*-1′ : 2′ : 4 : 3-1 : 2-α-*naphthapyrone*, m.p. 167°. Similarly, with $POCl_3$, orcinol affords 5-*hydroxy*-7-*methyl*- (VI), m.p. 215—216° (*acetate*, m.p. 107—108°), 4 : 6-diethylresorcinol, 5-*hydroxy*-6 : 8-*diethyl*-, m.p. 181—182°, phloroglucinol, 5 : 7-*dihydroxy*- (VII), m.p. 273° (*diacetate*, m.p. 133—134°), and pyrogallol, 7 : 8-*dihydroxy*-, m.p. 240° (*diacetate*, m.p. 118—119°), -4′-*methyl*cyclo*penteno*-1′ : 2′ : 4 : 3-*coumarin*. The coumarins (II)—(VII) with $Hg(OAc)_2$ afford 6 : 8-*bisacetoxymercuro*-derivatives. J. D. R.

Review of methods used for distinguishing chromones from coumarins. G. R. KELKAR (Rasāyanam, 1936, **1**, 68—74).—Chromones and coumarins can be distinguished by degradation to an *o*-OH-ketone or -acid or an *o*-methoxycinnamic acid, or, for 2-methylchromones, by formation of a styrene derivative, but negative results are in all cases inconclusive. R. S. C.

Syntheses in the 5-hydroxybenzopyrone group. I. 5-Hydroxy-2-methylchromone. D. B. LIMAYE and G. R. KELKAR (Rasāyanam, 1936, **1**, 24—29).—5-Hydroxy-3-acetyl-2-methylchromone (I) (A., 1936, 855) when boiled with dil. Na_2CO_3 or NaOH yields 5-*hydroxy*-2-*methylchromone*, m.p. 92° [isolated from dil. AcOH, or from the *Na* salt, also obtained from (I) and NaOEt] (*Ac*, m.p. 108—110°, and *Bz*, m.p. 149°, derivatives), hydrolysed (dil. NaOH) to γ-resorcylic acid. 2-Acetylresorcinol Me ether and NaOAc–Ac_2O at 160—170° give 5-*methoxy*-3-*acetyl*-2-*methylchromone*, m.p. 149—151°, demethylated ($AlCl_3$) to (I), and hydrolysed to 2-hydroxy-6-methoxybenzoic acid (J.C.S., 1915, **107**, 838). The above chromones do not condense with PhCHO, nor does 7-hydroxy-3-acetyl-2-methylchromone. 7-Hydroxy-2-methylchromone, however, gives a *benzylidene* derivative, m.p. 188—190°. E. W. W.

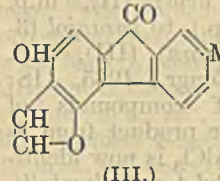
Influence of an acyl group in the 3-position on reactions of chromones. I. Action of aluminium chloride on 7-acetoxy-3-acetyl-2-methylchromone and a critical examination of the work of Wilson Baker. G. R. KELKAR and D. B. LIMAYE (Rasāyanam, 1936, **1**, 60—64).—Contrary to statements of Baker *et al.* (A., 1934, 410; 1935, 80), 7-acetoxy-3-acetyl-2-methylchromone is deacetylated by $AlCl_3$ in $PhNO_2$ to give 7-hydroxy-3-acetyl-2-methylchromone and thence by alkali yields an acid, decarboxylated to 1 : 3 : 2-$(OH)_2C_6H_3$·COMe, whilst 7-hydroxy-8-acetyl-2-methylchromone and aq. NaOH give 2 : 4-diacetylresorcinol. 3-Acetyl-*x*-acetoxy-2-methylchromones are hydrolysed in the Fries reaction, whereas similar chromones without the Ac in position 3 rearrange normally. R. S. C.

Monohydroxyphenylxanthens. J. B. NIEDERL and W. F. HART (J. Amer. Chem. Soc., 1937, **59**, 719—720).—Xanthhydrol and the appropriate phenol in AcOH at 100° or with H_2SO_4 at 0° or $AlCl_3$ in hot C_6H_6, followed, if necessary, by methylation, give 9-*p*-hydroxy-, m.p. 150° (Me ether, m.p. 112—113°; *benzoate*, m.p. 183—184°), -5′-*chloro*-2′-*hydroxy*-, m.p. 132°, and -2′-*hydroxy*-5′-*acetyl*-, m.p. 189°, -3′-*methoxy*-5′-tert.-*phenyl*isobutyl-, m.p. 210°, and -2′-*methoxy*-5′-tert.-β-*phenylamyl*-*xanthen*, m.p. 202°, and 1-*hydroxy*-x-*xanthylnaphthalene*, m.p. 195°. The products have PhOH coeff. <1. The compounds named have weak œstrogenic activity. R. S. C.

Synthesis of 1 : 2-3 : 4-dibenzoxanthone. E. GHIGI (Ber., 1937, **70**, [*B*], 742—744; cf. A., 1936, 1511).—9-Hydroxyphenanthrene (I) and *o*-OH·C_6H_4·CO_2H (II) are transformed by P_2O_5 in $CHCl_3$ into 9-*phenanthryl salicylate*, m.p. 142°, converted when rapidly heated into 1 : 2-3 : 4-dibenzoxanthone, m.p. 209°, also obtained in small yield and mixed with much PhOH and phenanthrene when a mixture of (I), (II), and Ac_2O is heated to dryness. Treatment of (I) with NaOMe and then with *o*-C_6H_4Cl·CO_2K and Cu powder at 150—200° gives a mixture of products among which diphenic acid is identified. H. W.

Anisoxide. I. R. W. JACKSON and R. F. SHORT (J.C.S., 1937, 513—516).—From star aniseed oil, *anisoxide* (I), $C_{14}H_{18}O$, m.p. 41°, b.p. 140°/11 mm., a highly unsaturated cyclic ether, has been isolated (additive *compound* with maleic anhydride, decomp. 280°). Catalytic reduction (H_2–PtO_2) of (I) gives *perhydroanisoxide* (II), b.p. 120—122°/10 mm., and reduction with Na–EtOH yields *dihydroanisoxide* (III), b.p. 120—122°/10 mm. Oxidation of (I) with air or O_3 affords MeCHO and with $KMnO_4$ gives an *acid*, $C_{12}H_{14}O_3$, m.p. 181—182° (*anilide*, m.p. 155—156°), further oxidised to an *acid*, $C_{11}H_{10}O_3$, m.p. 215—216°, and subsequently to an *acid*, $C_{11}H_{10}O_4$, m.p. 179·5—180·5° (*Me* ester, m.p. 79—80°), containing 1 OH. The oxide ring in (II) is broken by HBr to give a *dibromide*, $C_{14}H_{26}Br_2$, converted into the unsaturated *hydrocarbon*, $C_{14}H_{24}$, b.p. 110—112°/10 mm., which is oxidised (O_3) to a mixture from which a *ketone*, b.p. 102—105°/10 mm. (*semicarbazone*, m.p. 161—162°), is separated. (III) is oxidised ($KMnO_4$) to a ketone, $C_{14}H_{18}O_2$ (*semicarbazone*, m.p. 191—192·5°). A paraffin *hydrocarbon*, $C_{19}H_{40}$, m.p. 45—46°, has also been separated from the oil. F. R. S.

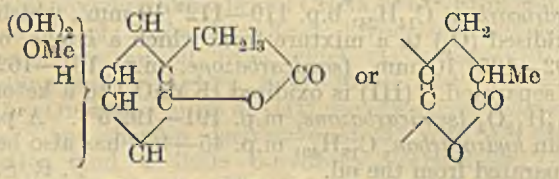
Syntheses in the naphthalene group. II. Heterocyclic analogues of the 4-hydroxy-1-aryl-2-naphthoic acids. W. BORSCHE and H. LEDITSCHKE (Annalen, 1937, **529**, 108—114).—Furyl *p*-tolyl ketone, b.p. 180—183°/23 mm., m.p. 41—42°, condenses with Et_2 succinate (I) to a dark brown resin which is cyclised by Ac_2O and NaOAc and then de-acetylated and hydrolysed to 4-*hydroxy*-1-*furyl*-6-*methyl*-2-*naphthoic acid*, m.p. 196—198° (*Me* ester, m.p. 206°), and 3-*hydroxy*-6-p-*tolylcoumarone*-5-*carboxylic acid* (II), m.p. 234° [*Ac* derivative, m.p. 238°; *Me* ester, m.p. 172°, and its *Ac* derivative, m.p. 120°; 3-*hydroxy*-4-*benzeneazo*-6-p-*tolylcoumarone*-5-*carboxylic acid*, m.p. 199° (decomp.)]. When heated in quinoline containing Cu bronze (II) passes into 3-*hydroxy*-6-p-*tolylcoumarone*, b.p. 170—172°/0·1 mm., m.p. 110°. With conc. H_2SO_4 at room temp. (II) gives 9-*keto*-7-*hydroxy*-2-*methyl*-5 : 6-2′ : 3′-*furanofluorene* (III), m.p. 278°. *Furyl* p-*anisyl ketone*, m.p. 63°, is transformed by (I) and NaOEt into b-*Et H* γ-2-*furyl*-γ-p-*anisylitaconate*, m.p. 146°, cyclised to 3-*hydroxy*-6-p-*anisylcoumarone*-5-*carboxylic acid*, m.p. 256°



(III.)

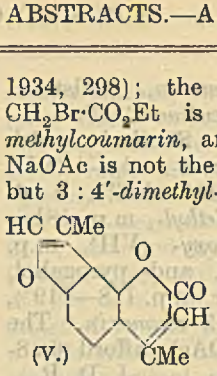
(*PhN*$_2$-derivative, decomp. 219°). (I) and *furyl* 3 : 4-*dimethoxyphenyl ketone*, m.p. 114°, yield a brown resin whence 3-*hydroxy*-6-3′ : 4′-*dimethoxyphenylcoumarone*-5-*carboxylic acid*, m.p. 272°. (I) and 2-benzoylthiophen give as non-cryst. H ester, transformed into non-cryst. 4-*hydroxy*-1′-2′-*thienyl*-2-*naphthoic acid* (*PhN*$_2$-derivative, decomp. 237°). H. W.

Luganin. I. K. W. Merz and K. G. Krebs (Arch. Pharm., 1937, **275**, 217—236).—Luganin (I) (isolated in 1·7% yield from the pulp of *Strychnos nux vomica*), $C_{16}H_{22}O_9$·OMe, m.p. 222—223° (decomp.; rapid heating), $[\alpha]_D^{20}$ −82·11° in H_2O [*Ac*$_5$, m.p. 142°, *Bz*$_5$, m.p. 157—158°, and (p-*NO*$_2$·*C*$_6$*H*$_4$·*CO*)$_5$ derivatives, m.p. 207—208°], has normal mol. wt. in H_2O, but not in other solvents. It contains a lactone group, neutralising 1 NaOH when heated, and its acyl derivatives consume 1 extra mol. of hot NaOH. It is hydrolysed by emulsin or acid to glucose (identified as osazone and penta-acetate) and *luganetin* (II), $C_{11}H_{16}O_5$, amorphous, $[\alpha]_D^{13\cdot5}$ −23·71° in EtOH, but heating during hydrolysis causes decomp. As usually obtained (II) is very hygroscopic, but repeated evaporation of its Et_2O solution gives a less sol., non-hygroscopic dimeride (?). It gives a (*CPh*$_3$)$_2$, m.p. 155—156°, *CPh*$_3$, m.p. 115—117°, and (p-*NO*$_2$·*C*$_6$*H*$_4$·*CO*)$_2$ derivative, m.p. about 110°; with Se it gives traces of a cryst. substance, with KOH–H_2O_2 gives HCO_2H, AcOH, and possibly $AcCO_2H$; it is destroyed by other oxidising agents, absorbs 1 H_2 catalytically, and reacts slowly with aq. Br, possibly by substitution. When heated, (II) absorbs 2 mols. of NaOH and its acyl derivative absorbs an excess of

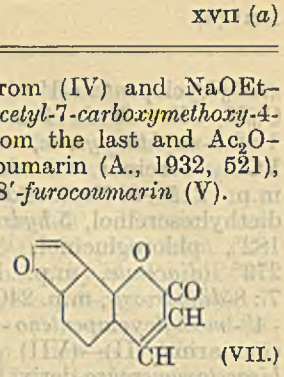


2 mols. Probably (II) is the lactone (above formulæ) of a phenolic acid, (I) being the lactone of an alcoholic acid with the phenolic OH glucosidically bound. R. S. C.

Syntheses in the furocoumarin group. II. The karanjelin way of synthesising furocoumarins as illustrated on 5 : 4 : 7′ : 8′-furocoumarin. D. B. Limaye. III. Formation of the linear 3 : 4′-dimethyl-4 : 5 : 6′ : 7′-furocoumarin. D. B. Limaye and D. D. Gangal (Rasāyanam, 1936, **1**, 1—14, 15—23).—II. Oil from the seeds of the leguminous plant karanja (*Pongamia glabra*) contains *karanjin*, identified as 3′-*methoxy*-2′-*phenyl*-5 : 4 : 7′ : 8′-*furochromone* (I), which is degraded through *karanjic acid* (3-*hydroxybenzfuran*-4-*carboxylic acid*) (II), m.p. 220° (decomp.), to *karanjol* (3-*hydroxybenzfuran*) (III), m.p. 55—56° (cf. Proc. Indian Sci. Congr., 1935, 118; 1926, 151). The synthesis of compounds of type (I) is attempted. The major product from 4-methylumbelliferone acetate and $AlCl_3$ is now identified (cf. A., 1932, 521) as 8-*acetyl*-4-*methylumbelliferone* (IV), since it gives 2-acetylresorcinol (cf. A., 1934, 298); the product from (IV) and NaOEt–CH_2Br·CO_2Et is thus 8-*acetyl*-7-*carboxymethoxy*-4-*methylcoumarin*, and that from the last and Ac_2O–NaOAc is not the *lin.*-furocoumarin (A., 1932, 521), but 3 : 4′-*dimethyl*-5 : 4 : 7′ : 8′-*furocoumarin* (V).



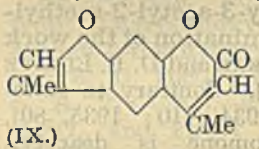
(V.)



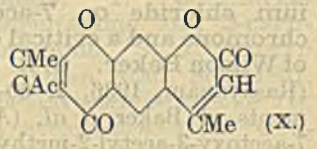
(VII.)

2 : 6-Dimethoxybenzaldehyde (A., 1935, 83) and $AlCl_3$–C_6H_6 at room temp. give 2-*hydroxy*-6-*methoxybenzaldehyde* (VI), m.p. 75° (*semicarbazone*, m.p. 250°), further demethylated to 2 : 6-*dihydroxybenzaldehyde*, m.p. 154—155°. With NaOEt–CH_2Br·CO_2Et, (VI) forms 2-*aldehydo*-3-*methoxyphenoxyacetic acid*, m.p. 138°, converted (Ac_2O–NaOAc at 150°) into 3-*methoxybenzfuran*, b.p. 220—222°, also obtained by methylation of (III). With aq. $NaHCO_3$ at 120°, (III) gives (II); with NaOH–$CHCl_3$, (III) yields 3-*hydroxybenzfuran*-4-*aldehyde*, m.p. 60° (*semicarbazone*, m.p. 253°). This with NaOAc–Ac_2O at 170° yields 5 : 4 : 7′ : 8′-*furocoumarin* (VII), m.p. 139—140°, of the same constitution as has been assigned (A., 1934, 780) to angelicin.

III. 4-Methylumbelliferone acetate and $AlCl_3$ at 160° yield [with 8-acetyl-4-methylumbelliferone (above)] 6-*acetyl*-4-*methylumbelliferone* (VIII), m.p. 210° (*semicarbazone*, m.p. >300°; *Me ether*, m.p. 209—210°; *Bz*, m.p. 160°, and *Ac*, m.p. 172°, derivatives), which with NaOEt–CH_2Br·CO_2Et (better yield from the *Na* derivative) gives 6-*acetyl*-7-*carbethoxymethoxy*-4-*methylcoumarin*, m.p. 183°. This is hydrolysed by NaOH–EtOH to the 7-*carboxymethoxy*-compound, m.p. 268—270° (decomp.), which is condensed by Ac_2O at 150—155° to the (linear) 3 : 4′-*dimethyl*-4 : 5 : 6′ : 7′-*furocoumarin* (IX), m.p. 222°. With Ac_2O–NaOAc at 150—160° (VIII) gives 5-*acetyl*-6 : 4′-*dimethyl*-2 : 3 : 7′ : 6′-(1 : 4-*pyrono*)-



(IX.)



(X.)

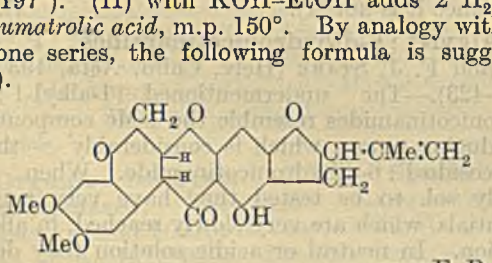
coumarin (X), m.p. 245°, hydrolysed to a *substance*, $C_{14}H_{12}O_5$, m.p. 262°, and an *acid*, m.p. 223—225°. E. W. W.

Syntheses in the furocoumarin group. IV. General considerations on the synthesis of the third type of furocoumarin from resorcinol. D. B. Limaye (Rasāyanam, 1936, **1**, 43—44; cf. preceding abstract).—General principles of this synthesis are discussed. R. S. C.

Identification of tephrosin and deguelin from different sources. J. J. Boam, R. S. Cahn, and A. Stuart (J.C.S.I., 1937, **56**, 91—96T).—*allo*-Tephrosin (I) (Merz *et al.*, A., 1935, 221) is impure tephrosin (II); *isoallo*tephrosin (III) is pure (II). *iso*Deguelin (IV) is identical with deguelin (V). *iso*Dehydrodeguelin is identical with dehydrodeguelin except in colour; the two forms are not interconvertible, but either may be given by most

methods of formation; the yellow colour of the *iso*-form resists removal by C, crystallisation, etc., as does that of dehydrorotenone, which is obtained in the ordinary yellow form from rotenolone-II by Ac_2O–NaOAc, one of the few reactions which always gives the colourless dehydro-compound in the deguelin series. Crystallo-optical data, which are detailed for these substances and for the substance, m.p. 189° (now named *sumatrol*), obtained from Sumatra-type *Derris* roots (Cahn *et al.*, B., 1935, 381), are essential for identification as m.p. are unreliable and variable in the rotenone series. Dihydrodeoxy*iso*-deguelin and dihydro*isoallo*tephrosin are correctly named *dihydrodeoxydeguelin* and *dihydrotephrosin*, respectively; dihydro*allo*tephrosin was an impure form of the latter. Other derivatives of (IV) are identical with those of (V), and those of (I) and (III) with those of (II). In the normal methods of prep. either (II) or (V) or mixtures of both may be obtained from one sample of *Derris* or *Lonchocarpus nicou* in different experiments. Purification of (II) by crystallisation is often ineffective and is best achieved by hot NaOH–EtOH or NH_3–EtOH. R. S. C.

Sumatrol. I. A. Robertson and G. L. Rusby (J.C.S., 1937, 497—503).—*Sumatrol* (I), $C_{21}H_{16}O_5(OMe)_2$, m.p. 194°, $[\alpha]_D$ −184° in C_6H_6, isolated from the resin of a species of *Derris* (cf. Cahn and Boam, B., 1935, 381), forms an *oxime*, m.p. 245—247°, cannot be dehydrated, and contains a phenolic OH *ortho* to CO. (I) is converted (I; Zn–AcOH) into *dehydrosumatrol* (II), m.p. 190—192°, $[\alpha]_D$ −55° in $CHCl_3$ (*Ac* derivative, m.p. 256—259°). Hydrogenation (H_2–Pt) gives *tetra*-, m.p. 222—223°, $[\alpha]_D$ +122° in $CHCl_3$, and *di-hydrosumatrol*, m.p. 184—185°, $[\alpha]_D$ −32° in $CHCl_3$. The H_2-compound is converted into *dehydrodihydrosumatrol*, m.p. 235°, $[\alpha]_D$ −63° in $CHCl_3$, and the H_4-compound into *dehydrotetrahydrosumatrol*, m.p. 218° (*Ac*$_2$ derivative, m.p. 197°). (II) with KOH–EtOH adds 2 H_2O to give *sumatrolic acid*, m.p. 150°. By analogy with the rotenone series, the following formula is suggested for (I).



F. R. S.

***l*-Asarinin, a new constituent of varieties of *Asarum*. I. Constitution of *l*-asarinin.** T. Kaku, N. Kutani, and J. Takahashi (Keijo J. Med., 1936, **7**, 644—656).—*Asarum sieboldi*, Miquel, and its variety *seoulensis*, Nakai, contain l-*asarinin*, $C_{20}H_{20}O_6$ (I), m.p. 122—123°, $[\alpha]_D^{20}$ −118·6° (all rotations in $CHCl_3$), which is not attacked by aq. KOH at the b.p., but with KOH–NaOH at 250° slowly yields protocatechuic acid. $KMnO_4$–Ac_2O gives piperonal and piperonylic acid, and HNO_3 (*d* 1·48)–AcOH forms *dinitro*-l-*asarinin*, m.p. 220—221°, $[\alpha]_D^{18}$ +30·6°, and 4-nitro-1 : 2-methylenedioxybenzene (II), new m.p. 148°; more energetic oxidation gives (II), 6-nitropiperonal, and $H_2C_2O_4$. EtOH–HCl partly isomerises (I) into l-*sesamin*, m.p. 122—124°, $[\alpha]_D^{17}$ −68·1°. Sesamin (A., 1929, 298) is renamed d-*sesamin*, and dl-*sesamin*, m.p. 129—130°, $[\alpha]_D$ 0°, is prepared. *Dinitro*-d-, m.p. 240—241°, $[\alpha]_D^{18}$ +35·1°, and -l-*sesamin*, m.p. 240—241°, $[\alpha]_D^{19}$ −34·5°, are obtained, with (II). *Dinitro*-dl-*sesamin*, m.p. 223°, has $[\alpha]_D$ 0°. d-*Sesamin* with EtOH–HCl at 100° is partly isomerised into d-*asarinin*, m.p. 122—123°, $[\alpha]_D^{19}$ +119·1° [$(NO_2)_2$-derivative, m.p. 220—221°, $[\alpha]_D^{17}$ −29·5°]; dl-*asarinin*, m.p. 135—136°, and *dinitro*-dl-*asarinin*, m.p. 223°, have $[\alpha]_D$ 0°. *l*-Asarinin is saturated, and does not contain a ketone group. The alternative structures $CHR<\begin{matrix}O—CH\cdot CHR\\ CH_2\cdot CH—O\end{matrix}>CH_2$ and $O<\begin{matrix}CH_2—CH\cdot CHR\\ CHR\cdot CH—CH_2\end{matrix}>O$ (R = $C_6H_3\cdot O_2CH_2$) are proposed. E. W. W.

Action of alkali disulphides on tetrabromotetramethylmethane. H. J. Backer and N. Evenhuis (Rec. trav. chim., 1937, **56**, 129—136).—Interaction of $C(CH_2Br)_4$ with K_2S_2 or Na_2S_2 in boiling EtOH affords 2 : 6 : 7-*trithia*-4-spiro*octane* 2-*sulphide* (I), $\begin{matrix}S—CH_2\\ S—CH_2\end{matrix}>C<\begin{matrix}CH_2\\ CH_2\end{matrix}>S{:}S$, m.p. 78·5°, which yields cryst. *compounds* +$HgCl_2$ and +$HgBr_2$ and when refluxed with Cu–PhMe gives 2 : 6 : 7-*trithia*-4-spiro-*octane*, m.p. 55·5—56·5° ($HgCl_2$ and $HgBr_2$ additive *compounds*). (I) is oxidised by BzO_2H in $CHCl_3$ to 2 : 6 : 7-*trithia*-4-spiro*octane* 2 : 2 : 6 : 6-*tetroxide*, m.p. 257° (decomp.), and H_2SO_4, and by H_2O_2–AcOH to 1-*thia*-3 : 3-*disulphodimethyl*cyclo*butane* 1 : 1-*dioxide* + $2H_2O$, $SO_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>C(CH_2\cdot SO_3H)_2,2H_2O$ (*Ba* salt + $3H_2O$; *Tl* salt). The corresponding 3 : 3-*dimethyldisulphonyl dichloride*, m.p. 144—146°, yields a *dianilide*, m.p. 200—202°. Similarly $CMe_2(CH_2Br)_2$ when refluxed (3 hr.) with K_2S_2–EtOH gives 4 : 4-*dimethyl*-1 : 2-*dithia*cyclo*pentane*, $CMe_2<\begin{matrix}CH_2\cdot S\\ CH_2\cdot S\end{matrix}$, b.p. 128—129°/27 mm., which polymerises to a white solid when heated and is oxidised by AcOH–H_2O_2 to ββ-*dimethylpropane*-αγ-*disulphonic acid* (*Tl* salt + H_2O), isolated as the *Ba* salt (+H_2O). H. G. M.

Catalytic transformation of heterocyclic compounds. VI. Comparison of action of catalysts in the simultaneous dehydration of furan and ammonia. J. K. Juriev and P. M. Rakitin (J. Gen. Chem. Russ., 1937, **7**, 485—491).—The activity of a no. of catalysts of the reaction of production of pyrrole (I) from furan and NH_3 at 350—600° falls in the order Al_2O_3>ThO_2>$MgSO_4$>C>Fe_2O_3; max. yields (40%) of (I) are obtained with Al_2O_3 at 550°. The mechanism of the reaction is discussed. R. T.

2-Methyl-4-*n*-amylpyrrole. F. Wrede (Arch. exp. Path. Pharm., 1937, **184**, 327—330).—Et *n*-octoylacetate (prep. from heptaldehyde) when treated with $NaNO_2$, reduced with Zn, and condensed with $CH_2Ac\cdot CO_2Et$ gave *Et*$_2$ 2-*methyl*-4-n-*amylpyrroledicarboxylate*, m.p. 85°, which when distilled over soda-lime yielded 2-*methyl*-4-n-*amylpyrrole* (I), b.p. 130°/10 mm., reduced (Pd–C–H_2 in AcOH) to 2-*methyl*-4′-n-*amylpyrrolidine* [*platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, m.p. 140°; *aurichloride*, an oil]. The pyrrole $C_{10}H_{17}N$

derived by oxidative breakdown of prodigiosin is not (I). P. W. C.

3-Aminopiperidine. H. NIENBURG (Ber., 1937, 70, [*B*], 635—638).—3-Aminopyridine hydrochloride is quantitatively reduced (PtO_2 in MeOH) to 3-*aminopiperidine dihydrochloride* (I), m.p. 225° after softening at 180° (corresponding *dipicrate*, decomp. 258°, and *platinichloride*, $C_5H_{12}N_2,H_2PtCl_6$), which is stable towards $KMnO_4$ at room temp. (I) and NaOEt in MeOH–EtOH yield 3-*aminopiperidine*, b.p. 68°/17 mm., 168—170°/760 mm., m.p. 55—57° [Bz_2, m.p. 197°, and *dicarbamyl*, m.p. 213° (decomp.), derivatives]. H. W.

Association of α-piperidone. G. I. JENKINS and T. W. J. TAYLOR (J.C.S., 1937, 495—497).—Measurements of apparent mol. wt. of α-piperidone in H_2O show little sign of association, but in C_6H_6 the val. is 1·75 times the formula wt. at low dilution and approximates to 2 as concn. increases. This indicates that the association takes place by H-bond formation to give a dimeric form. This is discussed with reference to the linkings in a polypeptide chain. F. R. S.

Conductivities and potentials of higher alkylpyridinium chlorides.—See A., I, 309.

"Acid fissions," particularly of certain pyridinium salts. F. KRÖHNKE and W. HEFFE (Ber., 1937, 70, [*B*], 862—878).—Study of the rate of fission of many phenacylpyridinium salts by NaOH at 20° shows that negative substituents in the *m*- or *p*-position in the C_6H_6 nucleus accelerate whereas positive substituents retard hydrolysis. Hydrolysis of salts which do not yield *o*-substituted aromatic acids depends on the dissociation const. of the latter. *o*-Substituents cause great retardation due to steric influences, the effect being particularly noticeable in the $C_{10}H_8$ series. Di-*o*-substituted compounds do not undergo hydrolysis. Fission is hampered by positive, facilitated by negative, substituents in the C_5H_5N nucleus. Hydrolysis occurs much more rapidly in H_2O than in EtOH. Salts substituted in the CH_2 by acyl residues are hydrolysed with difficulty by alkali, with ease by acids whereby acalkyl*cyclo*ammonium salts are produced. Salts substituted in the CH_2 by alkyl are much more readily hydrolysed than the unsubstituted salts; in this respect the phenacylpyridinium salts resemble 1 : 3-diketones, $CH_2Ac{\cdot}CO_2Et$, and many other compounds all of which contain the group :CX·C:O (X=S, N, or O). Phenacylpyridinium bromide is converted by dioxan (containing peroxides) into methylenedipyridinium bromide (H_2O_2 in neutral solution containing a suitable acceptor can oxidise Br′ to Br). The following *-phenacylpyridinium bromides* are described; p-*methyl*-, m.p. 205° (decomp.) [ω-*Br*-derivative, m.p. 180° (decomp.)]; 3-*nitro*-4-*methyl*-, m.p. 217—218° (decomp.); 3-*bromo*-4-*methyl*-, m.p. 215—217° (decomp.); 3 : 4-*dimethyl*-, m.p. 232—233° (decomp.); 2 : 4-*dimethyl*-, m.p. 210° (decomp.); 2 : 4 : 6-*trimethyl*-, m.p. 273° (decomp.) [*perchlorate*, m.p. 273° (decomp.); *nitrate*]; 2 : 3 : 5 : 6-*tetramethyl*-, decomp. >280° (corresponding *enol-betaine*, m.p. 190—191°); p-*methoxy*-, m.p. 203—204° (decomp.) (corresponding *perchlorate*, m.p. 199°, and *enol-betaine*, m.p. 96°); 3-*bromo*-4-*methoxy*-, m.p. 224—225° [corresponding *perchlorate*, m.p. 187—189°, and *enol-betaine*, m.p. 97° (incipient decomp. 93°)]; p-*phenoxy*-, m.p. 168—170°, and the corresponding *enol-betaine*, m.p. 105—108°; p-*nitro*-, m.p. 245—247° (decomp.); m-*chloro*-, decomp. about 250° (corresponding *perchlorate*, m.p. 198—199°); o-*chloro*-, m.p. 211° (decomp.) (corresponding *perchlorate*, m.p. 176—177°); o-*bromo*-, m.p. 213° (decomp.); 2 : 5-*dichloro*-, m.p. 271° (decomp.) (corresponding *perchlorate*, m.p. 237—238°); 2 : 6-*dichloro*-, m.p. 280—281° (decomp.) (corresponding *perchlorate*, decomp. >280°). 3-Bromopyridine and CH_2BzBr afford 3-*bromo*-1-*phenacylpyridinium bromide*, m.p. 209—211° (decomp.), which gives an *enol-betaine*, m.p. 118—119° (decomp.). 3-*Bromo*-1-p-*bromophenacylpyridinium bromide*, decomp. 245·5°, gives an *enol-betaine*, m.p. 134—135° (decomp.). *Phenacyl*-3 : 5-*dibromopyridinium bromide*, m.p. 220—221° (decomp.) (also *hydrate*) and the *enol-betaine*, decomp. 115°, are described. 2-Chloropyridine and CH_2BzBr yield *phenacyl*-2-*chloropyridinium bromide* ($+1H_2O$), m.p. 179°, transformed by NaOH into 1-*phenacyl*-2-*pyridone*, m.p. 154·5° (*perchlorate*, m.p. 131° after softening at 125°). *Phenacylpyridinium sulphate*, m.p 236°, and *H sulphate*, m.p. 203—204°, are described. p-iso*Propylphenacylpyridinium perchlorate* has m.p. 182·5°. H. W.

Manufacture of bases derived from 2-aminopyridine.—See B., 1937, 421.

Constitution of products of sulphonation of 3-amino- and 3-hydroxy-pyridine. E. PŁAZEK (Rocz. Chem., 1937, **17**, 97—100).—5-Nitro-2-thiolpyridine in aq. NH_3 and $KMnO_4$ at 100° yield chiefly the *K* salt of 5-*nitropyridine*-2-*sulphonic acid* (I), m.p. 302—304°, together with 5-*nitro*-2-*aminopyridine* (II), m.p. 186—188°, also obtained from (I) and $SnCl_2$. The product of sulphonation of 3-aminopyridine (A., 1934, 1009) must be 3-aminopyridine-2-sulphonic acid, since it is not (I). R. T.

1-Alkyl-1 : 6-dihydronicotinamides. P. KARRER and F. J. STARE (Helv. Chim. Acta, 1937, **20**, 418—423).—The undermentioned 1-alkyl-1 : 6-dihydronicotinamides resemble the 1-Me compound (I) in reducing power, which is considerably > that of 1-glucosido-1 : 6-dihydronicotinamide. When sufficiently sol. to be tested they have very negative potentials, which are very slowly reached, in alkaline solution. In neutral or acidic solution they decompose immediately giving non-cryst., very hygroscopic substances apparently formed by addition of acid which in the adduct is devoid of ionogenic properties. This property is explained by the presence of a conjugated system of double linkings which also permits the union with maleic anhydride to uninviting adducts. The absorption spectrum has a characteristic max. at 365 mμ. Nicotinamide is transformed by boiling EtI into the corresponding *ethiodide*, m.p. 198°, reduced by $Na_2S_2O_4$ and Na_2CO_3 to non-cryst. 1-*ethyl*-1 : 6-*dihydronicotinamide* and a *substance*, m.p. 220—230° (decomp.). The following are prepared analogously: *nicotinamide propiodide*, m.p. 182°, and 1-*propyl*-1 : 6-*dihydronicotinamide*, m.p. 96° after softening; *nicotinamide butiodide*, m.p. 152—153°, and 1-*butyl*-1 : 6-*dihydronicotinamide* which crystallises

when strongly cooled; *nicotinamide benzylchloride*, m.p. 236° (decomp.), and 1-*benzyl*-1 : 6-*dihydronicotinamide*, m.p. 123° after softening at about 115°; *nicotinamide cetochloride*, m.p. 235° (decomp.), and 1-*cetyl*-1 : 6-*dihydronicotinamide*, m.p. 54°.

[With J. F. BARTLETT.] (I) is hydrogenated (PtO_2 in H_2O) to 1-*methylhexahydronicotinamide*, m.p. 95°. H. W.

Oxidation product of adrenaline. D. RICHTER and H. BLASCHKO (J.C.S., 1937, 601—602).—The red product formed by oxidising *l*-adrenaline with KIO_3 has been isolated; it is probably 2-iodo-3-hydroxy-1-methyl-2 : 3-dihydroindole-5 : 6-quinone. F. R. S.

Organic catalysts. XV. Synthetic carboxylases. V. W. LANGENBECK and O. GÖDDE (Ber., 1937, **70**, [*B*], 669—671; cf. A., 1934, 1229; 1936, 1471).—The data 0·64, 1·48, 0·79, 0·20, 1·18, 1·59, 1·32, and 1·00 are recorded for the activity vals. of 5-aminonaphthoxindole, its 6-, 7-, and 8-OH- and 5-, 6-, 7-, and 8-Me derivatives, respectively. 1 : 4-$C_{10}H_6Me{\cdot}NH_2$ and $(OH)_2C(CO_2Et)_2$ in AcOH at room temp. yield *Et* 5-*methyl*-1-*naphthadioxindolecarboxylate*, m.p. 220° (decomp.), converted by successive hydrolysis, treatment with air, and acidification into 5-*methyl*-1-*naphthisatin*, decomp. (indef.) >230°, the *oxime*, m.p. 240°, of which is reduced by $SnCl_2$ and conc. HCl in AcOH at 100° to 3-*amino*-5-*methyl*-1-*naphthoxindole hydrochloride*. 1 : 5-$C_{10}H_6Me{\cdot}NH_2$ yields analogously *Et* 6-*methyl*-1-*naphthadioxindolecarboxylate*, m.p. 215° (decomp.), which gives successively 6-*methyl*-1-*naphthadioxindole*, 6-*methyl*-1-*naphthisatin*, m.p. 257° (decomp.), its *oxime*, m.p. 277°, and 3-*amino*-6-*methyl*-1-*naphthoxindole hydrochloride*, which is stable in air. 2 : 5-$C_{10}H_6Me{\cdot}NH_2$ affords successively *Et* 7-*methyl*-1-*naphthadioxindolecarboxylate*, m.p. 196° (decomp.), 7-*methyl*-1-*naphthisatin*, m.p. about 265° after darkening, 7-*methyl*-1-*naphthisatinoxime*, m.p. 274°, and 3-*amino*-7-*methyl*-1-*naphthoxindole hydrochloride*, decomp. >185°. Similarly, 2 : 8-$C_{10}H_6Me{\cdot}NH_2$ yields *Et* 8-*methyl*-1-*naphthadioxindolecarboxylate*, 8-*methyl*-1-*naphthisatin*, m.p. 254° (decomp.), 8-*methyl*-1-*naphthisatinoxime*, m.p. 250°, and 3-*amino*-8-*methyl*-1-*naphthoxindole hydrochloride*. H. W.

Organic catalysts. XVI. Synthetic dehydrogenases. III. W. LANGENBECK, L. WESCHKY, and O. GÖDDE (Ber., 1937, **70**, [*B*], 672—674; cf. A., 1927, 546).—The dehydrogenase activity towards *dl*-alanine of isatin-4- and -6-carboxylic acid is 20 times that of isatin (*loc. cit.*). Activity of the catalysts in enhanced 100-fold when dil. C_5H_5N containing some AcOH is substituted for dil. AcOH as solvent. The acids are nearly thrice as active as the yellow enzyme. H. W.

Derivatives of 3-nitro-4-hydroxyquinoline. M. COLONNA (Gazzetta, 1937, **67**, 46—53).—3-Nitro-4-hydroxyquinoline yields (Me_2SO_4 etc.) 3-*nitro*-4-*methoxy*-, m.p. 220°, -4-*ethoxy*-, m.p. 202°, -4-*propoxy*-, m.p. 156°, and -4-*butoxy-quinoline*, m.p. 140°, reduced (Sn–HCl) to 3-*amino*-4-*methoxy*- [*hydrochloride*, m.p. 155° (decomp.); *Ac* derivative, m.p. 216°], -4-*ethoxy*- [*hydrochloride*, m.p. 165° (resolidifying 168°, remelting 218°; *Ac* derivative, m.p. 160°], -4-*propoxy*- [*hydrochloride*, decomp. 215°; *Ac* derivative, m.p. 177—178°], and -4-*butoxy-quinoline* [*hydrochloride*, decomp. 283°; *Ac* derivative, m.p. 135—136°].

o-$NH_2{\cdot}C_6H_4{\cdot}CO_2Me$ in HCl with $NO_2{\cdot}CH_2{\cdot}CH{:}N{\cdot}OH$ yields *Me* o-β-*nitroethylideneaminobenzoate* (I), m.p. 153°, which when boiled with Ac_2O–NaOAc forms a *substance* [additive product of (I) and Ac_2O ?], m.p. 113—114°, hydrolysed (HCl) to (I), but does not condense to the quinoline. E. W. W.

Salts of bivalent silver. Quinolinate of Ag^{II}. (MLLE.) A. BURADA (Ann. Sci. Univ. Jassy, 1935, **20**, 71—74).—$C_5H_3N(CO_2)_2Ag,C_5H_3N(CO_2H)_2,2H_2O$ (I), which contains Ag^{II}, has been prepared by the oxidation of $Ag(C_9H_7N)_2NO_3$ by $(NH_4)_2S_2O_8$ or from $AgNO_3$ + quinolinic acid + $K_2S_2O_8$. It forms sparing sol. red crystals, gives a blue colour with $NHPh_2$ in H_2SO_4, oxidises alkali halides to halogens, AgCl being formed, and is decolorised by NH_3 and H_2O_2. R. S. B.

Acridine. XVI. Preparation of 2- and 4-substituted acridones from 3′-substituted diphenylamine-2-carboxylic acids. K. LEHMSTEDT and K. SCHRADER (Ber., 1937, **70**, [*B*], 838—849).—3′-Methoxydiphenylamine-2-carboxylic acid is transformed by $POCl_3$ at 100° into a mixture of 5-*chloro*-2-*methoxy*- (I), m.p. 170°, and 5-*chloro*-4-*methoxy*- (II), m.p. 124—125°, -*acridine*. (I) is converted by long heating with 20% H_2SO_4 at 100° into 2-*methoxyacridone*, m.p. 273°, whilst (II) with *N*-HCl readily affords 4-methoxyacridone, m.p. 346°. Ring-closure of the acid can also be effected by conc. H_2SO_4 at 100° but is accompanied by sulphonation, the effect of which is removed by after-treatment with boiling 50% H_2SO_4. 3′-Methyldiphenylamine-2-carboxylic acid gives a mixture of chloromethylacridines from which 2-methylacridone, m.p. 312°, is isolated by short treatment with *N*-HCl at 100°, whilst further heating of the filtrate leads to 4-*methylacridone*, m.p. 336°. 3′-Chlorodiphenylamine-2-carboxylic acid yields 2 : 5-dichloroacridine, m.p. 169—170°, and 4 : 5-*dichloroacridine*, m.p. 116—117°, converted by $NPhMe_2$ and $POCl_3$ at 100° into 4-*chloro*-5-p-*dimethylaminophenylacridine*, m.p. 252—253°, and by *N*-HCl into 4-*chloroacridone*, m.p. >360°. 3′-Nitrodiphenylamine-2-carboxylic acid affords 5-chloro-2-nitroacridine, m.p. 214°, and 5-*chloro*-4-*nitroacridine*, m.p. 140—141°, whence 4-*nitro*-5-p-*dimethylaminophenylacridine*, m.p. 280—281°, and 4-*nitroacridone*. 4-*Aminoacridone* blackens at about 275°. H. W.

Manufacture of 4 : 5-dihydroglyoxalines.—See B., 1937, 422.

Higher-melting crystals from solutions of picrolonic acid. L. KOFLER and F. A. MÜLLER (Mikrochem., Molisch Festschr., 1936, 271—273).—Solutions of technical picrolonic acid deposit small amounts of unknown crystals of two characteristic habits, (*a*) m.p. 200—250°, (*b*) decomp. 150—180°. J. S. A.

New synthetic method in the pyrazole group. I. R. FUSCO and R. JUSTONI (Gazzetta, 1937, **67**, 3—10).—Halogenohydrazones, CRX:N·NHR, and Na derivatives of cyanoketones, β-diketones, or β-ketonic esters, form pyrazoles. Thus α-chlorobenzaldehydephenylhydrazone (I) with the Na derivative of

$CN\cdot CH_2Ac$ gives *4-cyano-1 : 3-diphenyl-5-methylpyrazole*, m.p. 134°, hydrolysed to the *4-carboxylamide*, m.p. 232°, and thence to the acid; with $CN\cdot CH_2\cdot COBu^{\gamma}$ *4-cyano-1 : 3-diphenyl-5-tert.-butylpyrazole*, m.p. 163—164°, hydrolysed, with difficulty, to the *4-carboxylamide*, m.p. 211° [also obtained from (I) and the Na derivative of $COBu^{\gamma}\cdot CH_2\cdot CO\cdot NH_2$], which could not be further hydrolysed; and, with $CN\cdot CH_2Bz$, 4-cyano-1 : 3 : 5-triphenylpyrazole, hydrolysed to the *4-carboxylamide*, m.p. 197° (similarly obtained from $CH_2Bz\cdot CO\cdot NH_2$), and to the acid. E. W. W.

Sodium phenylethylbarbiturate solution for injection. L. Nielsen (Dansk Tidsskr. Farm., 1937, **11**, 65—77).—The decomps. 5-phenyl-5-ethylbarbituric acid + $H_2O \rightarrow CHPhEt\cdot CO\cdot NH\cdot CO\cdot NH_2$ (I) + CO_2, (I) + $H_2O \rightarrow CHPhEt\cdot CO_2H + CO(NH_2)_2$ (II), (II) + $H_2O \rightarrow CO_2 + 2NH_3$, $NH_2\cdot CO_2Et$ (III) + $H_2O \rightarrow CO_2 + NH_3 + EtOH$ (IV), (III) + $H_2O \leftarrow$ (IV) + (II) + CO_2, have been studied in solution at room temp. and 80°. Apparatus for the determination of small quantities of CO_2 is described. M. H. M. A.

Substituted barbituric acids.—See B., 1937, 499.

Multivalent amino-acids and peptides. VIII. Synthesis of bisanhydro-*l*-cystinyl-*l*-cystine and other diketopiperazines of cystine. (Miss) J. P. Greenstein (J. Biol. Chem., 1937, **118**, 321—329).—An attempt to prepare a polymeride of anhydrocysteinylcysteine in which dimethyldiketopiperazine rings would form a repeating pattern yielded only a dimeride. The acid chloride (I) from dicarbobenzyloxycystine combines in $CHCl_3$ with cysteine Et ester hydrochloride to form *Et$_2$ di(carbobenzyloxy)-l-cystyldi-l-cysteinate*, m.p. 72—76°, which with PH_4I yields *cysteinylcysteine Et ester hydriodide*, converted by NH_3–EtOH into *anhydro-l-cysteinyl-l-cysteine*, $SH\cdot CH_2\cdot CH<^{NH\cdot CO}_{CO\cdot NH}>CH\cdot CH_2\cdot SH$, m.p. 208° (decomp.), $[\alpha]_D^{23}$ −62·5° in H_2O (converted by cold conc. HCl into *cysteinylcysteine hydrochloride*, m.p. 158°, $[\alpha]_D^{22}$ +44·8°, oxidised to *cystinylcystine*). This is oxidised by H_2O_2 to *bisanhydro-l-cystinyl-l-cystine*, $[\cdot S\cdot CH_2\cdot CH<^{NH\cdot CO}_{CO\cdot NH}>CH\cdot CH_2\cdot S\cdot]_2$, decomp. (without melting) 250—310°, $[\alpha]_D^{23}$ +312·5° in H_2O (mol. wt. determined), hydrolysed (conc. HCl) to an 89% yield of cystine. (I) with Et_2 glutamate gives *Et$_2$ di(carbobenzyloxy)-l-cystyldi-l-glutamate*, m.p. 145°, converted by PH_4I into *Et$_2$ cysteinylglutamate hydriodide*; this with NH_3–EtOH at 0° gives a product which when aërated in H_2O containing NH_3 and $FeCl_3$ gives *Et$_2$ anhydro-l-cystyldi-l-γ-glutamate*, m.p. 259°. *Me$_2$ di(carbobenzyloxy)-l-cystyldi-l-glutamate*, m.p. 139°, similarly gives *Me$_2$ anhydro-l-cystyldi-l-γ-glutamate*, m.p. 258°. Similarly *Et$_2$ di(carbobenzyloxy)-l-cystyldi-l-aspartate*, m.p. 145°, gives *Et anhydro-l-cystyldi-l-β-aspartate*, m.p. 246°, and *Et$_2$ di(carbobenzyloxy)-l-cystyldityrosinate*, m.p. 168—175°, gives *anhydro-l-cystyldi-l-tyrosine*, m.p. 283° (decomp.). E. W. W.

Nitroso- and bromo-phenylpyriminazole. V. K. Matveev (Bull. Acad. Sci. U.R.S.S., 1936, 1005—1015).—*3-Nitroso-* (I), m.p. 163—164°, and *3-bromo-2-phenylpyriminazole* (II), m.p. 129—130°, prepared by the usual reactions, are described. Br and (I) yield (II). R. T.

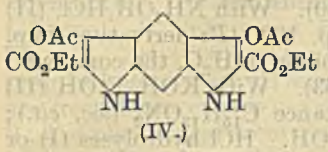
Metal carbonyls. XXIV, XXV. [Compounds of cobalt and nickel with *o*-phenanthroline and 2 : 2′-dipyridyl.]—See A., I, 322.

Chemiluminescent organic compounds. IV. Amino- and hydrazino-*cyclo*phthalhydrazides and their relative luminescent power. H. D. K. Drew and F. H. Pearman (J.C.S., 1937, 586—592).—3-Aminophthalimide with MeI–MeOH gives *N-methyl-3-dimethylaminophthalimide methiodide*, m.p. 204° (decomp.), from which MeI cannot be eliminated, and with Me_2SO_4 is obtained *3-methylaminophthalimide* (I), m.p. 218° [3-N-*Ac* derivative, m.p. 285° (decomp.)]. This with 1 mol. of N_2H_4 forms *N-amino-3-methylaminophthalimide*, m.p. 194°, transformed above the m.p. into 5-methylaminophthalaz-1 : 4-dione, m.p. 331° (decomp.) [5-N-*Ac* derivative, m.p. 329° (decomp.)], also obtained from (I) and 3 mols. of N_2H_4. 3 : 6-Dichlorophthalimide with aq. NH_3 and Cu_2I_2 forms *3 : 6-diaminophthalimide* (II), m.p. 298° (decomp.) [*Ac$_2$* derivative, m.p. 321° (decomp.)], which with N_2H_4 in H_2O yields *3 : 6-diamino-N-aminophthalimide*, m.p. 282° (+H_2O), and in EtOH affords *N-amino-3 : 6-diacetamidophthalimide*, m.p. 319° (decomp.) (*Ac* derivative, m.p. 248°) N_2H_4 and (II) yield *5 : 8-diaminophthalaz-1 : 4-dione*, m.p. 329° (decomp.) [+H_2O; *Ac$_2$* derivative, m.p. 279° (decomp.); *Ac$_3$* derivative, m.p. 306° (decomp.)]. (III) and NaOH, followed by HCl and Ac_2O, give *3 : 6-diacetamidophthalic anhydride*, m.p. 279°. *4 : 5-Dichlorophthalimide*, m.p. 221°, is obtained from the anhydride. 6 : 7-Dichlorophthalaz-1 : 4-dione, Cu_2I_2, and aq. NH_3 yield *6 : 7-diaminophthalaz-1 : 4-dione*, m.p. 340° [+$2H_2O$; *phenanthrazine* derivative (+$2H_2O$, m.p. >340°]. *Na phthalimide-3-hydrazine-β-sulphonate* (IV) is hydrolysed to *3-hydrazinophthalimide*, m.p. 216° and 208°, converted by N_2H_4 into *N-amino-3-hydrazinophthalimide*, m.p. 202°. N_2H_4 and (IV) in EtOH form *Na N-aminophthalimide-3-hydrazine-β-sulphonate*, and in H_2O afford *Na phthalaz-1 : 4-dione-5-hydrazone-β-sulphonate*, hydrolysed to *5-hydrazinophthalaz-1 : 4-dione*, m.p. 312° (decomp.). Pyromellitic dianhydride and N_2H_4 give *pyromellitaz-1 : 4 : 6 : 9-tetraone* [*Na* salt (+$4H_2O$)].

Fluorescence occurs in the phthalimides and *cyclo*hydrazides containing NH_2 *ortho* to the junction of the rings, but not in those containing *m*-NH_2. The *N*-aminophthalimides derived from fluorescent phthalimides are non-fluorescent; this is not due to the removal of the imide-H, but is an effect of the *N*-NH_2 itself, since fluorescence persists in the *N*-methyl- and *N*-phenyl-phthalimides. The luminescent power of the substances described has been compared; only the phthalaz-1 : 4-diones show chemiluminescence, the 5-ring compounds giving no visible light in any instance. The open-chain hydrazides glow only when transformation into 6-ring hydrazides has taken place. F. R. S.

Heterocyclic compounds containing nitrogen. XXIX. Derivatives of *m*- and *p*-phenylenediamine and of 6-amino-oxindole. P Ruggli and R. Grand (Helv. Chim. Acta, 1937, **20**, 373—386; cf. this vol., 214).—*m*-$C_6H_4(NH_2)_2$ and $CHBr(CO_2Et)_2$

at room temp. give *Et*$_2$ m-*phenylenediaminomalonate* (I), m.p. 79°. Et$_2$ p-*phenylenediaminomalonate* (II), m.p. 108°, and *Et*$_2$ *benzidinedimalonate* (III), m.p. 134°, are obtained analogously. (I) loses EtOH at 205—220° and the product is acetylated to *Et*$_2$ 3 : 5-*diacetoxybenzodipyrrole*-2 : 6-*dicarboxylate* (IV), m.p. 180°, which does not give an indigoid dye when melted with KOH; the yield is poor.



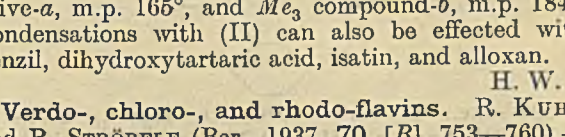
(IV.)

Attempted ring-closure with (II) or (III) gives only amorphous products. A ring-closure under milder conditions and from simpler reactants is illustrated by the production of *Et* 2 : 5-*diketo*-1 : 3-*diphenyltetrahydroglyoxaline*-4-*carboxylate*, m.p. 134·5°, from PhNCO and NHPh·CH(CO$_2$Et)$_2$ at 145°. *p*-Phenylenediglycine appears to yield polymerised products when treated successively with $SOCl_2$ and $AlCl_3$. *m*-$C_6H_4(NH_2)_2$ and CH_2BzBr in Et_2O–EtOH afford *di*-m-*phenacylaminobenzene*, m.p. 164°, in modest yield; it resinifies so readily that its prep. in quantity is difficult. *Di*-p-*phenacylaminobenzene* (V), m.p. (indef.) 151° (*picrate*, m.p. 124°; *Ac*$_2$ derivative, m.p. 227°), forms salts with acidic reagents (HCl–AcOH; conc. H_2SO_4) and does not yield cryst. compounds with the customary amine hydrochlorides. *m*-NO_2·C_6H_4·NH_2 and CH_2BzBr afford m-*nitrophenacylaniline*, m.p. 168°, which could not be cyclised. p-*Acetamidophenacylaniline*, m.p. 173°, from CH_2BzBr, *p*-NH_2·C_6H_4·NHAc, and Na_2CO_3 in EtOH at 50°, yields (V) when hydrolysed with AcOH and conc. HCl containing a little Zn dust and is cyclised by *p*-NH_2·C_6H_4·NHAc,HCl at 170—175° to 5-*acetamido*-2(or 3)-*phenylindole*, m.p. 217°. *Et* 2 : 4-*dinitrophenylacetate*, b.p. 200—210°/13 mm., is reduced (H_2–Ni–EtOH–EtOAc–H_2O) to *Et* 2 : 4-*diaminophenylacetate*, m.p. 75° [*Ac*$_2$, m.p. 190°, and *Bz*$_2$, m.p. 161°, derivatives; *picrate*, decomp. (indef.) 165—215°]. Acidification and evaporation of the reduced solution gives 6-amino-oxindole hydrochloride in 78% yield, whence 6-amino-oxindole (VI), m.p. about 200° (decomp.). 6-p-*Toluenesulphonamidooxindole*, m.p. 228—229°, is transformed by NaOH and Me_2SO_4 into N-*methyl*-6-p-*toluenesulphonamidooxindole*, m.p. 253°, and ON-*dimethyl*-6-p-*toluenesulphonamido-oxindole*, m.p. 203°; the latter substance is hydrolysed by 80% H_2SO_4 at 135—150° to 5-*amino*-ON-*dimethyloxindole*, m.p. 165—166°, the *NO*-derivative, m.p. 137°, of which could not be reduced to the corresponding hydrazino-compound. (VI) is converted by CH_2Cl·COCl in Et_2O–dioxan at 0° into 6-*chloroacetamido-oxindole*, decomp. >270°, which is completely decomposed by $AlCl_3$–NaCl at 170—190°. (VI) and Ac_2O in C_6H_5N afford 6-*acetamido-oxindole*, decomp. >335°, transformed by HNO_3 (*d* 1·51) at −12° to 0° into 5(?)-*nitro*-6-*acetamido-oxindole*, decomp. 250—300°, which does not give defined products when reduced, hydrolysed, and then treated with HCO_2H or AcOH. H. W.

Preparation of 2-phenylpyriminazole. V. K. Matveev (Bull. Acad. Sci. U.R.S.S., 1936, 533—542; cf. Tschitschibabin, A., 1926, 1153).—2-Phenylpyriminazole (*oxalate*, decomp. at 195°; *sulphate*, m.p. 190°) is obtained in theoretical yield from 2-aminopyridine (I) and phenacyl chloride or bromide (II) in aq. $NaHCO_3$ at room temp.; the reaction is supposed to take place between the pyridonimine form of (I) and the enol form of (II). R. T.

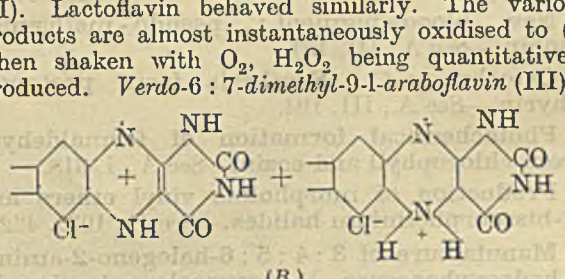
Lumazines and alloxazines. R. Kuhn and A. H. Cook (Ber., 1937, 70, [*B*], 761—768).—The compound, CH:N·C·NH·CO / CH:N·C·CO·NH or CH·N:C·NH·CO / CH·N:C·CO·NH, although previously designated alloxazine, is now termed *lumazine* (I) since the former nomenclature is now customary for the tricyclic system. Addition of a solution of trimeric glyoxal in warm H_2O to a hot aq. solution of 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate (II) gives (I), m.p. >350°, which under the Hg-vapour lamp gives bluish-green, green, and blue fluorescence in neutral, alkaline, and acid solution, respectively. It is converted by CH_2N_2 into a yellow product which resinifies in air; 1 : 3-dimethyl-lumazine is not obtained from the *Ag* salt and MeI. Polymeric AcCHO and (II) give *methyllumazine*, m.p. >340°, probably a mixture of the 6- and 7-Me compounds, whilst 6 : 7-*dimethyl-lumazine*, m.p. >340°, is derived from (II) and Ac_2. Condensation of *p*-benzoquinone with (II) could not be effected whereas β-naphthaquinone gives a mixture of the isomeric 1′ : 2′-*naphthalumazine*-a (1 : 3-*Me*$_2$ derivative, m.p. 258—260°) and 1′ : 2′-*naphthalumazine*-b, m.p. >330° [1 : 3-*Me*$_2$ derivative, m.p. 304° (decomp.)]. Phenanthraquinone and (II) afford 9′ : 10′-*phenanthralumazine* (whence 1 : 3-*dimethyl*-5 : 6-7 : 8-*dibenzalloxazine*, m.p. 337°), also obtained from 9 : 10-diaminophenanthrene dihydrochloride and alloxan tetrahydrate (III) in dil. AcOH. 3 : 4-$(NH_2)_2C_6H_3$·CO_2H and (III) give a mixture of alloxazine-6- and -7-carboxylic acid, converted by CH_2N_2 into the *Me*$_3$ derivative-*a*, m.p. 165°, and *Me*$_3$ compound-*b*, m.p. 184°. Condensations with (II) can also be effected with benzil, dihydroxytartaric acid, isatin, and alloxan. H. W.

Verdo-, chloro-, and rhodo-flavins. R. Kuhn and R. Ströbele (Ber., 1937, 70, [*B*], 753—760).—6 : 7-Dimethyl-9-*l*-araboflavin (I) passes through three well-defined stages in its reduction to the leucoflavin



(*A*.)

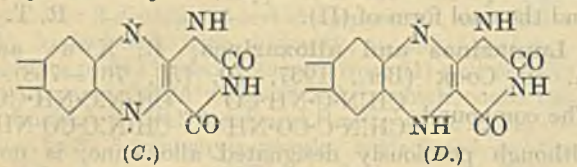
(II). Lactoflavin behaved similarly. The various products are almost instantaneously oxidised to (I) when shaken with O_2, H_2O_2 being quantitatively produced. *Verdo*-6 : 7-*dimethyl*-9-*l*-*araboflavin* (III) is



(*B*.)

obtained as the *Na* salt when (I) in 0·1*N*-NaOH is catalytically hydrogenated or reduced with $Na_2S_2O_4$. It is brownish-green and since it is paramagnetic the

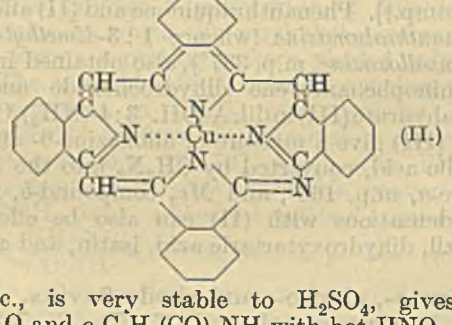
structure *A* is assigned to (III). In conc. HCl (III) dissolves to a blood-red solution of *rhodo*-6 : 7-*dimethyl*-9-l-*araboflavin*, isolated as the carmine-red



(*C.*) (*D.*)

dihydrochloride (IV) of constitution *B*. When washed with H_2O in absence of air (IV) is hydrolysed to a very sensitive brown base, converted by air into grass-green *chloro*-6 : 7-*dimethyl*-9-l-*araboflavin*, probably *C*, predominatingly dimeric; the formulation with N^{II} is based on Wieland's observations on substituted hydrazines. For (II) the structure *D* is established by the isolation of monoacetyldihydro-compounds from various flavins. H. W.

Action of cuprous cyanide on *o*-halogeno-acetophenones. J. H. Helberger (Annalen, 1937, **529**, 205—218).—*2-Bromo-4-methylacetophenone*, b.p. 130°/12 mm., is obtained from $CH_2Ac{\cdot}CO_2Et$ and 2 : 4-$C_6H_3BrMe{\cdot}COCl$, and 1-*chloro*-2-*acetylnaphthalene*, m.p. 53°, b.p. 175°/12 mm., from 1 : 2-$C_{10}H_6Cl{\cdot}COCl$. *o*-Bromo- or -chloro-acetophenone with CuCN in quinoline at 210—220° give the *Cu* derivative (II) of *tetrabenzoazaporphin*, a violet salt, which sublimes at



(II.)

>500°/vac., is very stable to H_2SO_4, gives *o*-$C_6H_4(CO)_2O$ and *o*-$C_6H_4(CO)_2NH$ with hot HNO_3, has a 6-banded absorption spectrum, and generally resembles the phthalocyanines. Formation of this compound involves formation of *o*-$C_6H_4(CN)_2$ during the reaction; addition of a little dinitrile to the reaction mixture leads, however, to the *Cu* derivative of *tetrabenzodiazaporphin*, $C_{34}H_{18}N_6Cu$. The mono-azaporphin synthesis appears to be general, but the products in three analogous cases were more difficult to purify. R. S. C.

New blood-pigment: pseudo-methæmo-globin.—See A., III, 194.

Cytochrome-*C*. Synthesis from protoporphyrin.—See A., III, 194.

Photochemical formation of formaldehyde from chlorophyll and eosin.—See A., I, 318.

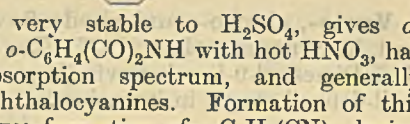
Production of morpholine vinyl ethers and *N*-bismorpholinium halides.—See B., 1937, 422.

Manufacture of 3 : 4 : 5 : 6-halogeno-2-amino-1-hydroxybenzenes [benzoxazolones].—See B., 1937, 420.

Action of semicarbazide hydrochloride on oximinotriphenylpyrrole. VI. T. Ajello (Gazzetta, 1937, **67**, 55—68).—Oximinotriphenylpyrrole and semicarbazide hydrochloride yield the semicarbazone (I), m.p. 227°, of 3-*benzoyl*-4 : 5-*diphenyl-isooxazole* (II), m.p. 158°, together with $(NH{\cdot}CO{\cdot}NH_2)_2$, aminotriphenylpyrrole, and triphenylpyrrolylhydroxylamine (cf. this vol., 30). With NH_2OH,HCl, (II) gives an *oxime* (III), m.p. 162° (*Bz* derivative, m.p. 122°), or, on prolonged boiling in H_2O, the compound $C_{22}H_{16}O_2N_2$ (A., 1935, 763). With KOH–EtOH (II) or (III) forms the substance $C_{15}H_{12}ON_2$ (*loc. cit.*); with KOH, (II) gives BzOH. HCl hydrolyses (I) or (III) to (II). E. W. W.

Condensation of isatin with phenols. I. α-Naphthol. J. O. Gabel and V. M. Zubarovski (J. Gen. Chem. Russ., 1937, 7, 305—310).—Isatin and α-$C_{10}H_7{\cdot}OH$ at 110—120° in presence of $POCl_3$ yield 2-keto-3 : 3-bis-α-naphthoxyindoline (*Ac* derivative, m.p. 273°), whilst in AcOH at the b.p. the product is 2-*keto*-3-(3′ : 4′-*benzo*-9′-*xanthyl*)*indoline*, m.p. 360° (*Ac* derivative, m.p. 305°). R. T.

Behaviour of ethyl thiazole-5-carboxylate methiodide on reduction. H. Erlenmeyer, A. Epprecht, and H. von Meyenburg (Helv. Chim. Acta, 1937, **20**, 514—515).—The *substance*, m.p. 153°, is unchanged by H_2 in PO_4''' solution (p_H 7·5) in presence of Pt-black at atm. pressure whereas Et nicotinate methiodide readily absorbs H_2 under these conditions. With $Na_2S_2O_4$–$NaHCO_3$ reaction is



H. W.

Thiazole and thiadiazine formation from thiosemicarbazones. J. McLean and F. J. Wilson (J.C.S., 1937, 556—559).—$CH_2Cl{\cdot}COMe$ (I) reacts with the Na salt of the appropriate thiosemicarbazone (PhCHO, $COMe_2$, and COPhMe, respectively) to give 2-*keto*-4-*methyl*-2 : 3-*dihydrothiazole*-2-*benzylidene*-, m.p. 190° (*hydrochloride*, m.p. 131°), -*isopropylidene*-, m.p. 90° or 115°, and -α-*phenylethylidene*-*hydrazone*, m.p. 134° (*hydrochloride*, m.p. 154°). Hydrolysis of these compounds with 0·1*N*-HCl yields 2-keto-4-methyl-2 : 3-dihydrothiazole-2-hydrazone, isolated as the *picrate*, m.p. 192°, and with conc. HCl forms 2-*amino*-5-*methyl*-1 : 3 : 4-*thiadiazine hydrochloride*, m.p. 228° (*picrolonate*, m.p. 235°). The corresponding *base*, m.p. 109°, is obtained from (I) and thiosemicarbazide, forms Ac_3, m.p. 167°, and Bz_2 derivatives, m.p. 201—202°, and reacts with CS_2 and PhNCS to yield respectively 2-*amino*-5-*methyl*-1 : 3 : 4-*thiadiazine* 5-*methyl*-1 : 3 : 4-*thiadiazine*-2-*dithiocarbamate*, decomp. 142°, and 2-*anilinothioformamido*-5-*methyl*-1 : 3 : 4-*thiadiazine*, m.p. 200° (decomp.). $CH_2Cl{\cdot}CHO$ with acetone- and benzaldehyde-thiosemicarbazone affords respectively 2-*keto*-2 : 3-*dihydrothiazole*-2-iso-*propylidene*-, m.p. 140°, and -*benzylidene*-*hydrazone*, m.p. 169°. F. R. S.

Rings containing nitrogen and sulphur. H. Wuyts (Bull. Soc. chim. Belg., 1937, **46**, 27—45).—A review of recent work on the carbodithioic acids, $R{\cdot}CS_2H$, and the prep. from them of aromatic aldehydes, tetrazines, indole derivatives, thio- and glycothio-diazolines. A. Li.

Recent work in alkaloid chemistry. A. P. Orekhov (Bull. Acad. Sci. U.R.S.S., 1936, 935—955).—A lecture. R. T.

Tobacco alkaloids. XII. Occurrence of *dl*-nornicotine, *dl*-anatabine, and *l*-anabasine in tobacco. E. Späth and F. Kesztler (Ber., 1937, **70**, [*B*], 704—709).—The mother-liquors from the prep. of *l*-nornicotine (I) diperchlorate (A., 1935, 1387) are freed by successive use of *l*- and *d*-6 : 6′-dinitro-2 : 2′-diphenic acid from the optically active isomerides as far as possible and an optically inactive product is obtained by suitable admixture of the feebly active bases derived from the respective salts. This gives a homogeneous, optically inactive 2 : 4-*dinitrobenzoyl* derivative, m.p. 159—160°, identical with that derived from 2 : 4-$(NO_2)_2C_6H_3$·COCl and authentic *dl*-nornicotine (II). Since (I) is not readily racemised it is probable that (II) exists pre-formed in tobacco and is not formed by racemisation of (I) during extraction. A sample of German tobacco contained almost exclusively optically homogeneous (I) whereas *d*-nornicotine from Australian *Duboisia Hopwoodii*, Muell, is more than half racemised.

Crystallisation of the diperchlorate of crude *l*-anatabine from H_2O leads to the isolation of *dl*-*anatabine perchlorate*, m.p. 129—130° (corresponding *dipicrate*, m.p. 201—201·5°; *trinitro*-m-*tolyloxide*, m.p. 140—141°; *dipicrolonate*, m.p. 233—235°). The constitution of the free *base* (III) is established by its dehydrogenation to 2 : 3′-dipyridyl, by the oxidation of its *Bz* derivative to BzOH, nicotinic and hippuric acid, and by its resolution into its optical antipodes. Since (III) is racemised with difficulty, it probably exists pre-formed in the plant. The isolation of *l*-anabasine, identical with that obtained from *Anabasis aphylla*, from the mother-liquors from (III) is described. H. W.

Alkaloids of *Salsola richteri*. A. P. Orekhov and N. F. Proskurnina (Bull. Acad. Sci. U.R.S.S., 1936, 957—960).—Salsolidine, $[\alpha]_D$ −53°, is the *O*-Me ether of *l*-salsoline, $[\alpha]_D$ −44°. R. T.

Alkaloids of different varieties of *Senecio*. R. A. Konovalova (Bull. Acad. Sci. U.R.S.S., 1936, 961—967).—Platyphylline, from *S. platyphyllus*, is hydrolysed to platynecinic acid and platynecine, $C_8H_{13}N(OH)_2$, the dichloride of which is hydrolysed to heliotridane. R. T.

Alkaloids of *Senecio*. III. Jacobine, jacodine, and jaconine. G. Barger and J. J. Blackie (J.C.S., 1937, 584—586).—Jacobine (*nitrate*, m.p. 234°, $[\alpha]_D^{17}$ −28·6° in H_2O) is the principal alkaloid of *Senecio* (cf. Manske, A., 1932, 286); it is hydrolysed to retronecine and jaconecic acid. From material collected in June and July, but not in that in August, *jacodine*, $C_{18}H_{25}O_5N$, m.p. 217°, $[\alpha]_D^{17}$ −109·6° in $CHCl_3$ (*nitrate*, m.p. 215°, $[\alpha]_D^{17}$ −77·4° in H_2O), and *jaconine*, $C_{18}H_{25}O_8N,H_2O$, m.p. 146°, have been isolated. F. R. S.

Synthesis of cocaine from hyoscyamine. M. N. Schtschukina, R. A. Lapina, and N. A. Preobrashenski (Bull. Acad. Sci. U.R.S.S., 1936, 997—1004).—See A., 1936, 1131. Hyoseyamine and H_2O (5 hr. at the b.p.) give tropine in 88·5% yield. R. T.

M.p. of cocaine hydrochloride. A. L. Dragan-esco (J. Pharm. Chim., 1937, [viii], **25**, 389—391).—The m.p. (to clear liquid) varies from 179° (heated during 60 min.) to 186·5° (26 min.), being 182—183° if the bath is kept const. at 170° and then heated at 2° per min. A. Li.

Constituents of *Lunasia costulata*. H. Dieterle and H. Beyl (Arch. Pharm., 1937, **275**, 276).—Lunacrine is $C_{16}H_{19}O_3N$ (cf. this vol., 216). R. S. C.

Roots of *Aristolochia indica*, Linn. III. Isolation of the alkaloid aristolochine. P. R. Krishnaswamy and B. L. Manjunath (J. Indian Chem. Soc., 1937, **14**, 39—41).—Aristolochine (A., 1935, 1433) is $C_{17}H_{19}O_3N$ and has $[\alpha]_D^{25}$ −268·6° [in MeOH ?]; it contains OMe and NMe_2. With PhMe and C_6H_6, it gives additive *compounds* (cf. *loc. cit.*), m.p. 159° (decomp.), and 163° (decomp.), respectively, both decomposed by MeOH. Its hydrochloride has $[\alpha]_D^{25}$ −236·2°; the *hydrobromide*, m.p. 262°, *picrate*, decomp. 222°, and *picrolonate*, m.p. 232° (decomp.) are prepared. E. W. W.

Alkaloids of fumariaceous plants. XII. *Corydalis scouleri*, Hk. XIII. *Corydalis sibirica*, Pers. R. H. F. Manske (Canad. J. Res., 1936, **14**, B, 347—353, 354—359).—XII. The following alkaloids are isolated (see A., 1933, 728) from the whole plant *C. scouleri*, Hk.: protopine (I) (0·15%), cryptopine (II) (0·004%) α-*allo*cryptopine (0·001%), bicuculline (III) (0·20%), scoulerine (IV) (0·06%), capnoidine (0·12%) (A., 1933, 841), corlumine (V) (0·12%) and corlumidine (0·02%) (this vol., 80), *alkaloid*-η (0·002%), $C_{21}H_{21}O_6N$, m.p. 180°, probably isomeric with adlumine and (V), and *alkaloid*-θ (VI) (0·002%), $C_{16}H_{17}O_3N$, m.p. 183° (methylation *product*, m.p. 162°).

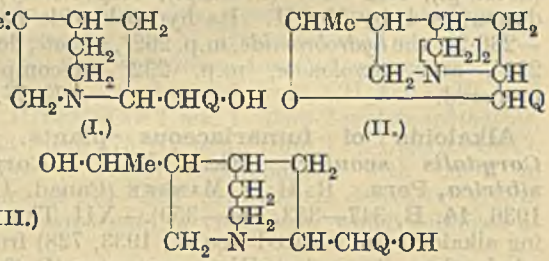
XIII. From *C. sibirica*, Pers., are isolated (I) (0·47%), (III) (0·10%), traces of (II), (IV), (V), and (VI), three new non-phenolic alkaloids, *alkaloid*-κ $C_{19}H_{17}O_5N$ + MeOH, m.p. 139° [*hydrochloride*, sinters 238—242°, m.p. 247° (decomp.)], -λ, $C_{19}H_{19}O_5N$, m.p. 212°, and -μ, $C_{18}H_{17}O_5N$, m.p. 236°, the last two each containing 2 OMe; and a phenolic *alkaloid*-ι, $C_{21}H_{21}O_4N$, m.p. 248°, containing 1 OMe. All m.p. are corr. J. W. B.

Isomerism of norcoralydine. G. Hahn and W. Kley (Ber., 1937, **70**, [*B*], 685—688).—The discrepancies between the observations of Pictet and Chou (A., 1916, i, 418) and Späth and Kruta (A., 1929, 201) are explained by the observation that norcoralydine exists in an α-form, m.p. 146° (hydrochloride, m.p. 218—220°; orange-red picrate, m.p. 138—140°), and a β-variety, m.p. 158° (hydrochloride, m.p. 213°; pale-yellow picrate, m.p. 109—110°). The forms do not differ greatly in stability since either form may separate from hot EtOH or Et_2O. Isolation of pure forms can be effected only by microscopical observation of the process of crystallisation with removal of the crystals at a suitable instant. H. W.

Narcotoline, a new alkaloid of the poppy (*Papaver somniferum*). F. Wrede (Arch. exp. Path. Pharm., 1937, **184**, 331—335).—*Narcotoline*,

$C_{21}H_{21}O_7N$, m.p. 202°, $[\alpha]_D^{20}$ −188° in $CHCl_3$, +5·8° in 0·1*N*-HCl [*tartrate*, $C_{21}H_{21}O_7N,C_4H_6O_6,0{\cdot}5H_2O$, sinters 120°, decomp. 200°, α 0°; *acetate hydrochloride*, $+H_2O$, m.p. 230—233° (decomp.), $[\alpha]_D^{20}$ +94·8° in H_2O], gives the same colour reactions as narcotine (I), contains one less OMe group than (I), is converted into (I) by CH_2N_2, and gives meconine when heated in a sealed tube with AcOH. P. W. C.

Modified cinchona alkaloids. IV. Constitution. T. A. Henry, W. Solomon, and E. M. Gibbs (J.C.S., 1937, 592—601).—The substances described as produced by the action of boiling 60% H_2SO_4 on quinine and quinidine are of three kinds: (*a*) isomerides of the two alkaloids, (*b*) demethylated (phenolic) bases corresponding with these isomerides, and (*c*) hydration products of *a* and *b*. It is possible to account for the reactions of many of them on the basis of formulæ (I), (II), and (III).



(I.) (II.)

(III.)

"Phenolic base *A*" (cf. A., 1935, 1136) is *neo*apo*quinidine* [(I) Q = 6-*hydroxyquinolyl*], m.p. 260°, $[\alpha]_D^{15}$ +206·2° or 120·7° in EtOH [*hydrochloride*, m.p. 197°, $[\alpha]_D^{15}$ +110·4°; *dihydrochloride*, m.p. 255° (decomp.), $[\alpha]_D^{15}$ +167·0°; *nitrate*, m.p. 100° (decomp.), $[\alpha]_D^{15}$ +102·2°; *neutral sulphate*, m.p. 80° or 218—220° (decomp.)]. Neo*iso*quinidine (*loc. cit.*) is a mixture of *neoisoquinidine* [(I) Q = 6-methoxyquinolyl], m.p. 83°, $[\alpha]_D^{15}$ +198·6° or 98·7° in EtOH [*nitrate*, m.p. 220° (decomp.), $[\alpha]_D^{15}$ +100·6°], and *ψ-quinidine*, m.p. 150—155° [+EtOH, m.p. 85—90°; *hydrochloride*, m.p. 269° (decomp.); *nitrate* m.p. 217—218° (decomp.)]. *apo*Quinidine Me ether is hydrogenated to dihydroquinidine and epi-C_3-*dihydroquinidine*, m.p. 151—152°, $[\alpha]_D^{15}$ +233·8°. α- and γ-*iso*Quinidines belong to type (II) (cf. Domanski *et al.*, A., 1935, 1137). Other transformation products of quinidine, analogous to those from quinine, are α-, m.p. 205° $[\alpha]_D^{15}$ +252·6° or +204·7° in EtOH (*hydrochloride*, m.p. 203—204°, $[\alpha]_D^{15}$ +165·3°), and β-*hydroxydihydro*apo*quinidine* [(III) Q = 6-hydroxyquinolyl] (+EtOH), m.p. 190° (decomp.), $[\alpha]_D^{20}$ +197° in EtOH [*hydrochloride*, m.p. 300° (decomp.), $[\alpha]_D^{15}$ +201·0° in H_2O], and *hydroxydihydroquinidine* [(III) Q = 6-*methoxyquinolyl*], m.p. 257°, $[\alpha]_D$ +298·5° or 225·3° in EtOH [*hydrochloride*, m.p. 277° (decomp.), $[\alpha]_D^{15}$ +198·6°].

*iso*apoQuinine and CH_2N_2 give α-*iso*quinine (*iso*apoquinine Me ether), m.p. 192—194°, $[\alpha]_D^{15}$ −364·3° or −253·4° in EtOH. β-*iso*Quinine is hydrogenated to epi-C_3-*dihydroquinine*, m.p. 169° [*dihydrobromide* (+$3H_2O$), decomp. 234°, $[\alpha]_D^{15}$ −184°], also obtained from α-*iso*quinine. These quinine derivatives belong to type (I).

The hydroxydihydro*apo*quinine previously described (*loc. cit.*) is designated the α-compound, and β- and γ-compounds have now been isolated. These substances belong to type (III). β-*Hydroxydihydro*apoquinine, m.p. indefinite, $[\alpha]_D^{15}$ −205·1°, [*dihydrobromide*, decomp. 245°, $[\alpha]_D^{15}$ −141·9°; *hydrochloride*, decomp. 255—260°; *sulphate*, m.p. 265—270° (decomp.)]. The α-compound is methylated (CH_2N_2) to a *base*, $C_{20}H_{26}O_3N_2$, m.p. 247—249°, $[\alpha]_D^{15}$ −197·5° or −119·1° in EtOH [*hydrochloride* (+$2H_2O$), m.p. 255—259° (decomp.), $[\alpha]_D^{15}$ −94·6° in EtOH]; *nitrate* (+H_2O), m.p. 226° (decomp.), $[\alpha]_D^{15}$ −103·8° in EtOH]. *allo*Quinidine (cf. Ludwiczak *et al.*, A., 1936, 490) is impure hydroxydihydroquinidine. F. R. S.

***Strychnos* alkaloids. XCIII. The acid $C_{15}H_{18}O_6N_2$ from benzylidenedihydrobrucine.** H. Leuchs and H. Beyer (Ber., 1937, 70, [*B*], 628—631; cf. A., 1934, 1237).—Oxidation (CrO_3; = 33 O) of the acid $C_{23}H_{26}O_7N_2$ from benzylidenedihydrobrucine yields the *acid* (I), $C_{15}H_{18}O_6N_2$, m.p. >310°, $[\alpha]_D^{21}$ −16°±5°, and a substance isolated as the *perchlorate*, $C_{17}H_{22}O_6N_2,HClO_4$, decomp. 260—275° (block). (I) is converted by boiling 5% HCl–MeOH into the *Me*$_2$ ester [*hydrochloride* (+0·5H_2O), m.p. 98—100°] and by similar treatment with HCl–EtOH into the *Et H* ester [*hydrochloride* (+0·5EtOH), m.p. 180—220°, decomp. 240—250°, $[\alpha]_D^{20}$ +21·8° in H_2O]. Reduction (PtO_2 in H_2O at 20—60°) of (I) gives the *H*$_2$-*acid* (II), $C_{15}H_{20}O_6N_2$, decomp. about 305° after darkening at 295°, $[\alpha]_D^{20}$ −52·1°, which does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$; (I) therefore contains the group ·CO·CO·N:. (II) yields an *Et H* ester (*hydrochloride* $C_{17}H_{24}O_6N_2,HCl,H_2O,0{\cdot}5EtOH$, $[\alpha]_D^{20}$ −18·2° in H_2O) and the presence of ·CH(OH)·CO·N: in it is established by the formation of an *Ac* derivative [*perchlorate*, $C_{17}H_{22}O_7N_2,HClO_4$, m.p. 150—160° (decomp.), $[\alpha]_D^{20}$ −8·7°]. H. W.

Mitraversine. Raymond-Hamet and L. Millat (J. Pharm. Chim., 1937, [viii], **25**, 391—398).—Extraction of the bark of *Mytragyna diversifolia*, Hook, with C_6H_6, followed by acidification (HCO_2H), repeated pptn. with K_2CO_3, and crystallisation from Et_2O and $COMe_2$, gives a cryst. *alkaloid*, m.p. 263·5—264·5° (corr.), apparently identical (except that it has only one OMe) with the mitraversine, $C_{20}H_{20}N_2O_2(OMe)_2$ of Field (J.C.S., 1921, **119**, 887—891), but different from mitranermine and mitraphylline; and an amorphous alkaloid, $C_{19}H_{20}N_2O_3(OMe)_2$, possibly a mixture. A. Li.

New alkaloid from the Rubiaceæ. Rubradinine. P. Denis (Bull. Acad. roy. Belg., 1937, [v], **23**, 174—182).—1% tartaric acid at 50° extracts from the bark *rubradinine*, $C_{24}H_{28}O_4N_2$, m.p. 306° (block) [*picrate*, m.p. 166° (block)], which occurs in the leaves, fruit, and stems. Many colour and pptn. reactions are described. J. L. D.

New alkaloid, formosanine, from *Ourouparia formosana*, Matsumura and Hayata. Raymond-Hamet (Compt. rend., 1936, **203**, 1383—1384).—*Formosanine* is $C_{24}H_{24(26)}O_4N_2$, m.p. 202—218° depending on rate of heating, [α] +91·3° in $CHCl_3$, +80·3° in EtOH. It contains 1 OMe and gives no coloration with H_2SO_4 or HNO_3, but a series of colour changes occurs with Mandelin's reagent. J. N. A.

Organo-arsenic compounds. P. S. YANG (Sci. Rep. Nat. Univ. Peking, 1936, **1**, No. 4, 1—8).—A review. J. D. R.

Arsinated derivatives of mixed ketones. (MISS) R. E. OMER and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, **59**, 642—644).—Resorcinol and PrCN give (Hoesch) a 65% yield of 2 : 4-dihydroxypropiophenone and thence the *Me*$_2$ *ether*, m.p. 67°, *Ac*$_2$, m.p. 89°, and 5-*NO*$_2$-derivative, m.p. 131° (*Me*$_2$ *ether*, m.p. 177°), and 5-*amino*-2 : 4-*dihydroxypropiophenone*, m.p. 147—151° (decomp.) (*Me*$_2$ *ether*, m.p. 107°). 5-*Nitro*-, m.p. 142°, and 5-*amino*-2 : 4-*dihydroxyacetophenone*, m.p. 137—142° (decomp.) (*Me*$_2$ *ether*, m.p. 114°), are similarly prepared. The amine *hydrochlorides* have m.p. >300°. The dihydroxyaminoketones give very poor, the dimethoxyaminoketones good, yields of 2 : 4-*dimethoxy*-5-*arsino*-*acetophenone*, m.p. 250°, and -*propiophenone*, m.p. 243°. R. S. C.

Structure and toxicity of arsinic acids of the diphenylamine series. V. A. ISMAILSKI and A. M. SIMONOV (J. Gen. Chem. Russ., 1937, **7**, 499—507).—The following substituted nitro- and amino-diphenylamine-4-arsinic acids have been prepared by the reactions: NH_2R + 4-chloro-3-nitrophenylarsinic acid + NaOH → $R{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}AsO_3H_2$ → (+ $Na_2S_2O_4$) $R{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}AsO_3H_2$: 3′-*acetamido*-, 3′-*hydroxy*-, 2′- and 3′-*methoxy*-, 4′-*ethoxy*-, 2-*nitro*-4′-p-*aminophenyl*-, and 3′-*acetamido*-, 4′-*hydroxy*-, and 4′-*ethoxy*-2-*amino*-*diphenylamine*-4-*arsinic acid*. Lowering of toxicity and intensification of colour are greater when R is in the 3′ than in the 4′ position. R. T.

Colour of 2-nitrodiphenylamine-4-arsinic acid derivatives containing additional auxo-groups. I. Auxo-enoid systems separated from the chromophore. V. A. ISMAILSKI and A. M. SIMONOV (J. Gen. Chem. Russ., 1937, **7**, 508—512; cf. preceding abstract).—The influence of substituents on the colour of diphenylamine-4-arsinic acid derivatives is discussed. R. T.

Diarsyls. VIII. Amino- and hydroxy-diarsyls. F. F. BLICKE and G. L. WEBSTER (J. Amer. Chem. Soc., 1937, **59**, 537—539).—2 : 2′-Diaminotetraphenylarsyl oxide (I) and *o*-aminodiphenylarsine, b.p. 218—220°/35 mm. (from *o*-aminodiphenylarsinic acid, Hg–Zn dust, and aq. HCl), in EtOH and N_2 give 2 : 2′-*diaminotetraphenyldiarsyl*, m.p. 133—135°, also obtained together with $(AsPh_2)_2$ from (I) and $AsHPh_2$, which absorbs O_2 readily in PhBr. 3 : 3′-Diaminotetraphenylarsyl oxide and 50% H_3PO_2 + a little HI afford 3 : 3′-*diaminotetraphenyldiarsyl*, m.p. 146—148°. *m*-Hydroxydiphenylarsinic acid and H_3PO_2 similarly give 3 : 3′-*dihydroxytetraphenyldiarsyl*, m.p. 134—136°, methylated (Me_2SO_4, aq. NaOH) to the 3 : 3′-(*OMe*)$_2$-derivative, m.p. 98—99°. These diarsyls react readily with O_2 in COPhMe. 3 : 3′-*Diamino*-4 : 4′-*dihydroxydiphenyldimethyldiarsyl*, m.p. 184—185° (*dihydrochloride*, m.p. 168—170°), is prepared from 3-amino-4-hydroxyphenylmethylarsinic acid and H_3PO_2 (cf. Bertheim, A., 1915, i, 331). *o*-Methoxydiphenyliodoarsine reacts rapidly with mol. Ag in C_6H_6 to give the oily diarsyl. All m.p. are in sealed tubes in N_2. H. B.

Tetra-arylphosphonium chlorides. N. N. MELNIKOV, A. E. KRETOV, and B. I. MELTZER (J. Gen. Chem. Russ., 1937, **7**, 461—463).—PPh_3 and CH_2RX in C_6H_6 at the b.p. yield the following phosphonium *salts*, of the general formula PPh_3RX: X = Cl, R = Ac, m.p. 234° (decomp.); X = Br, R = Ac, m.p. 221°; X = Br, R = Bz, m.p. 253° (decomp.); X = Cl, R = *o*-, m.p. 230° (decomp.), *m*-, m.p. 247° (decomp.), and *p*-$C_6H_4{\cdot}NO_2$, m.p. 247° (decomp.); X = Cl, R = *p*-$C_6H_4{\cdot}CN$, m.p. 244—245°. R. T.

2 : 6-Diselena-4-*spiro*heptane and other selena-*cyclo*butanes. H. J. BACKER and H. J. WINTER (Rec. trav. chim., 1937, **56**, 492—509).—K_2Se (I) and $C(CH_2Br)_4$ in EtOH–C_6H_6 give 2 : 6-*diselena*-4-spiro*heptane*, m.p. 67° (*mercurichloride*; *tetraiodide*, [unstable]), which, with MeI affords 3-*iodomethyl*-3-*methylselenolmethyl*-1-*selena*cyclo*butane methiodide* $Se<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}CH_2I\\CH_2SeMe_3I\end{matrix}$, m.p. 112—113° (*picrate*, m.p. 113—113·5°). $CMe_2(CH_2Br)_2$ with (I) in EtOH yields 3 : 3-*dimethyl*-1-*selena*cyclo*butane* (II), b.p. 56°/40 mm. [*di-iodide* (unstable); *mercuri-chloride* and *-iodide*], which, with MeI yields *dimethyl*-γ-*iodo*-ββ-*dimethylpropylselenonium iodide*, m.p. 105° [*platinichloride*, m.p. 167°; *aurichloride*, m.p. 98°; *picrate*, m.p. 114·5—115°]. Br or Cl_2 converts (II) into γ-*bromo*-ββ-*dimethylpropylselenium tribromide*, m.p. 103° (decomp.), and γ-*chloro*-ββ-*dimethylpropylselenium trichloride*, m.p. 100° (decomp.), respectively, converted by AgOH into γ-*bromo*-, m.p. 91°, and γ-*chloro*-ββ-*dimethylpropylselenious acid* (III), m.p. 90—91°. Oxidation (H_2O_2) of (II) affords 3 : 3-*dimethyl*-1-*selena*cyclo*butane* 1 : 1-*dioxide*, m.p. 132—132·5°, also obtained from the Na salt of (III) in EtOH. *cyclo*Hexanone with Na and $CH_2Cl{\cdot}CO_2Et$ in EtOH afford γ-*pentamethylene*-βγ-*epoxyethylpropionate*, b.p. 126°/15 mm., hydrolysed (NaOH) to the acid, which with HCl yields hexahydrobenzaldehyde; this with CH_2O yields 1 : 1-bishydroxymethyl*cyclo*hexane (improved method), converted by PBr_3 into 1 : 1-*bisbromomethyl*cyclo*hexane* (IV), b.p. 139·5°/17 mm. With (I) in EtOH, (IV) affords 2-*selena*-4-spiro*nonane* (V), b.p. 103·5—104°/13 mm., m.p. —46° (*mercuri-chloride* and *-bromide*), which with MeI affords γ-*iodo*-β-*pentamethylenepropyldimethylselenium iodide* (*picrate*, m.p. 121—121·5°). (V) in AcOH with I yields 2 : 2-*di-iodo*-2-*selena*-4-spiro*nonane*, m.p. 59° (decomp.), and with Br in CCl_4, 1-*bromomethyl*-1-*tribromoselenium*-*methyl*cyclo*hexane*, m.p. 121—122° (decomp.), converted by AgOH into γ-*bromo*-ββ-*pentamethylenepropylselenious acid*, m.p. 102·5—103°, the Na salt of which in EtOH affords 2-*selena*-4-spiro*nonane* 2 : 2-*dioxide*, m.p. 50—55°. With Cl_2 in CCl_4, (V) gives 1-*chloromethyl*-1-*trichloroselenium*-*methyl*cyclo*hexane*, m.p. 102—104°, converted by AgOH into γ-*chloro*-ββ-*pentamethylenepropylselenious acid*, m.p. 100—100·5° (decomp.). J. D. R.

Synthetic immunochemistry. I. Synthesis of *O*-β-glucosidotyrosine and its introduction into the protein molecule. R. F. CLUTTON, C. R. HARINGTON, and T. H. MEAD (Biochem. J., 1937, **31**, 764—771).—An attempt is made to prepare an

artificial compound antigen in which the carbohydrate group is attached to the protein through a naturally occurring type of chemical linking. O-β-*Glucosidotyrosine* (I), m.p. 282° (decomp.), $[\alpha]_{5161}$ −77°, is prepared by condensing acetobromoglucose with *N*-carbobenzyloxytyrosine Et ester, hydrolysis of the formed O-*tetra-acetyl*-β-*glucosido*-N-*carbobenzyloxytyrosine Et ester* (II), m.p. 108°, with $Ba(OH)_2$ giving O-β-*glucosido*-N-*carbobenzyloxytyrosine*, m.p. 177°, $[\alpha]_D$ −24·2°, and subsequent reduction with Pd–H_2. Emulsin hydrolyses (I). The *hydrazide* of (II) has m.p. 215°, $[\alpha]_D$ −37·5°, and when treated with HNO_2 yielded the *azide* and this was then coupled directly with gelatin (III) in alkaline solution to give O-β-*glucosido*-N-*carbobenzyloxytyrosylgelatin*. The carbobenzyloxy-groups were removed by treating the solution in anhyd. liquid NH_3 containing NH_4OAc with Na. Electrometric titration showed that no appreciable degradation of (III) had occurred. O-β-*Glucosidotyrosylgelatin* contained 4·6% of glucose and evidence is presented that in it the glucosidotyrosine residues are attached to the α-NH_2-groups of the (III). P. W. C.

Structure of proteins. IV. Benzoylated protein.—See A., III, 245.

Microchemical contributions [to qualitative analysis]. XIV.—See A., I, 326.

Manometric method for enzymic determination of arginine.—See A., III, 139.

Microdetermination of rubidium and cæsium in organic compounds. H. Roth (Mikrochem., 1937, **21**, 227—230).—The material is evaporated down with H_2SO_4, and Rb and Cs are finally weighed as sulphates. J. S. A.

Determination of nitrogen in diazo-compounds. H. Roth (Mikrochem., Molisch Festschr., 1936, 375—378).—Certain diazo-compounds (*e.g.*, the diazoketones of unsaturated acids) are decomposed catalytically by CuO at room temp., thus giving low vals. for N. Such materials are weighed in a Sn foil capsule, which is embedded in the CuO tube filling. J. S. A.

(A) **Use of liquid amalgams for analysis of hydroxy-nitro-compounds.** M. I. Perrier and M. M. Lobunetz. (B) **Determination of dinitrobenzene.** M. M. Lobunetz, (C) **Determination of nitro-group of nitrobenzene.** M. I. Perrier and M. M. Lobunetz. (D) **Analysis of nitrosalicylic acid.** M. M. Lobunetz (Bull. Sci. Univ. Kiev, 1936, **2**, 45—50, 69—72, 73—79, 81—83).—(A) 0·6—0·8 g. of *p*-nitrophenol in 4*N*-HCl is reduced by Zn–Hg to *p*-nitroaniline, which is titrated with 0·2*N*-$NaNO_2$.

(B) 15 c.c. of Zn–Hg are added to 0·3—0·4 g. of $C_6H_4(NO_2)_2$ in MeOH, followed by 40 c.c. of 4*N*-HCl, the mixture is shaken, and the aq. $C_6H_4(NH_2)_2$ is diluted to 200 c.c. 1 g. of KBr, 25 c.c. of 0·2*N*-$KBrO_3$, and 5 c.c. of 4*N*-HCl are added to 25 c.c. of solution, the mixture is shaken, and 8 c.c. of 40% KI are added after 15 min. The I liberated is titrated with $Na_2S_2O_3$.

(C) $PhNO_2$ is determined analogously to $C_6H_4(NO_2)_2$.

(D) Nitrosalicylic acid is determined analogously to nitrophenol. R. T.

Detection of ethylvanillin (bourbonal). P. Stadler and K. Wagner (Z. anal. Chem., 1937, **108**, 161—167).—The blue coloration given by ethylvanillin (I) with $FeCl_3$, unlike that given by vanillin (II), changes to a green colour at 60°. N_2H_4,H_2SO_4 + HCl gives ppts. of characteristic cryst. form with (I) and (II), that from (II) being luminescent in ultraviolet light. *p*-NO_2·C_6H_4·NH·NH_2 also gives characteristic ppts. (I), but not (II), gives a white ppt. when boiled with $NaNO_2$ + HNO_3. (I) when present alone may be determined by the gravimetric, volumetric, and colorimetric methods applicable for (II). J. S. A.

Determination of benzoic acid. F. W. Edwards, H. R. Nanji, and M. K. Hassan (Analyst, 1937, **62**, 172—177).—Nicholls' method (A., 1928, 313) is modified, notably to avoid the necessity for controlled acidity, by extracting the salicylic acid (I) formed in Et_2O and determining it colorimetrically with $FeCl_3$. The Jorissen test as modified by Nicholls (*loc. cit.*) is preferred for the determination of (I) in admixture with BzOH, whilst BzOH is detected by the Illing–Mohler test (A., 1932, 632) and determined by Nicholls' method after selective oxidation of (I) by alkaline $KMnO_4$ and extraction in Et_2O (cf. following abstract). J. G.

Detection and determination of *p*-hydroxybenzoic acid and its derivatives, with special reference to their distinction from salicylic and benzoic acids. F. W. Edwards, H. R. Nanji, and M. K. Hassan (Analyst, 1937, **62**, 178—185).—The NH_4 salts of the acids are obtained after extraction with Et_2O and hydrolysis of esters with KOH in EtOH, and a scheme is provided enabling the acids to be identified from the results obtained with the Millon, $FeCl_3$, Jorissen, Cu salt, Nicholls, and Illing–Mohler tests (cf. preceding abstract). *p*-OH·C_6H_4·CO_2H is determined colorimetrically, using Millon's reagent; in presence of salicylic acid the shade must be matched against that given by one of a series of mixtures of the two acids. Procedures for dealing with cordials, fatty foods, and meat and fish products are described. J. G.

Solubility of semicarbazones in dilute hydrochloric acid.—See A., I, 298.

2 : 3 : 7-Trihydroxy-9-methyl-6-fluorone, special reagent for antimony cations.—See A., I, 330.

Identification of different barbituric acids with Millon's reagent. M. Paget and Tilly (J. Pharm. Chim., 1937, [viii], **25**, 222—223).—The characteristic reactions of ten substituted barbituric acids with Millon's agent are tabulated. E. H. S.

Functional chemistry of morphine. New colour reaction for morphine and its pseudolic derivatives. J. A. Sanchez (J. Pharm. Chim., 1937, [viii], **25**, 346—351).—All derivatives with *sec.* alcohol group in ring 1 of Gulland and Robinson's formula, but no others, give a stable red-violet colour on boiling the solid with vanillin–HCl solution. R. M. M. O.